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Pollution Control Technical Manual for Koppers-Totzek Based Indirect Coal Liquefaction

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16. ABSTRACT

The document is one of six technical handbooks prepared by EPA to help government officials granting permits to build synfuels facilities, synfuels process developers, and other interested parties. They provide technical data on waste streams from synfuels facilities and technologies capable of controlling them. Process technolgies covered in the manuals include coal gasification, coal liquefaction by direct and indirect processing, and the extraction of oil from shale. The manuals offer no regulatory guidance, allowing the industry flexibility in deciding how best to comply with environmental regulations.

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POLLUTION CONTROL TECHNICAL MANUAL
FOR
KOPPERS-TOTZEK-BASED INDIRECT COAL LIQUEFACTION

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DISCLAIMER

This Pollution Control Technical Manual was based on data obtained in EPA's source characterization study at the Koppers-Totzek based plants at Modderfontein, S.A. and Ptolemais, Greece. The evaluation at Ptolemais was a joint study supported by the Tennessee Valley Authority (TVA) and the Environmental Protection Agency (EPA). Additional data sources used in this manual included other EPA synfuels characterization studies, environmental impact statements, published literature, and EPA supported engineering calculations. No proprietary or confidential data appear or have been used in the preparation of this manual. Although this manual addresses the Koppers-Totzek gasifier based technology, the process developer, Krupp-Koppers, GmbH, Essen was not involved in the development of this manual. Thus, the manual does not necessarily represent Krupp-Koppers' engineering design data, material balances, or operational information.

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The purpose of the Pollution Control Technical Manuals (PCTMs) is to provide process, discharge, and pollution control data in summarized form for the use of permit writers, developers, and other interested parties. The PCTM series covers a range of alternate fuel sources, including coal gasification and coal liquefaction by direct and indirect processing, and the extraction of oil from shale.

The series consists of a set of technical volumes directed at production facilities based upon specific conversion processes. The entire series is supplemented by a pollution control technology appendix volume which describes the operation and application of approximately 50 control processes.

All PCTMs are prepared on a base plant concept (coal gasification and liquefaction) or developer proposed designs (oil shale) which may not fully reflect plants to be built in the future. The PCTMs present examples of control applications, both as individual process units and as integrated control trains. These examples are taken in part from applicable permit applications and, therefore, are reflective of specific plants. None of the examples are intended to convey an Agency endorsement or recommendation but rather are presented for illustrative purposes. The selection of control technologies for application to specific plants is the exclusive function of the designers and permitters who have the flexibility to utilize the lowest cost and/or most effective approaches. It is hoped that readers will be able to relate their waste streams and controls to those presented in these manuals to enable them to better understand the extent to which various technologies may control specific waste streams and utilize the information in making control technology selections for their specific needs.

The reader should be aware that the PCTMs contain no legally binding requirements or guidance, and that nothing contained in the PCTMs relieves a facility from compliance with existing or future environmental regulations or permit requirements.

Herbert L. Wiser
Acting Deputy Assistant Administrator
Office of Research and Development
U.S. Environmental Protection Agency

ABSTRACT

The Environmental Protection Agency (EPA), Office of Research and Development has undertaken an extensive study to determine synthetic fuel plant waste stream characteristics and to evaluate potentially applicable pollution control systems. The purpose of this and all other PCTMs is to convey this information in a manner that is readily useful to designers, permit writers, and the public.

The Koppers-Totzek (K-T)-based indirect liquefaction PCTM addresses the K-T gasification technology as licensed by Krupp-Koppers, GmbH, Essen, West Germany (Gesellschaft fur Kohle-Technologie for licensing within the U.S.) and all intermediate process operations leading to each of three liquid product configurations. The liquid product syntheses considered include Fischer-Tropsch liquids, methanol, and Mobil M-gasoline. A single feed coal (Illinois No. 6 bituminous) is utilized throughout the manual as the basis for illustration, with the impacts of alternative coal ranks also described in the text.

This manual proceeds through a description of the hypothetical base plant, characterizes the waste streams produced in each medium, and discusses the array of commercially available controls which can be applied to the base plant waste streams. From these generally characterized controls, several examples are constructed for each medium in order to illustrate typical control technology applications. Then, example control trains are constructed for each medium, illustrating the function of integrated control systems. Control and control system cost and performance estimates are presented, together with descriptions of the discharge streams, secondary waste streams, and energy requirements. A summary of the gaps and limitations in the data base used to develop this manual is presented, along with a listing of additional data needs.

CONTENTS

FOREWORD iii
ABSTRACT iv
FIGURES viii
TABLES x
GLOSSARY OF ACRONYMS xv
CONVERSION FACTORS xviii
ACKNOWLEDGEMENT xviii

SECTION 1 INTRODUCTION 1

1.1 Koppers-Totzek Based Indirect Liquefaction 2
1.2 Approach to Manual Development 4
1.2.1 Base Plant Definition 4
1.2.2 Control Technology Evaluation 5
1.3 Data Base 6
1.4 Manual Organization and Utilization 9
1.4.1 Manual Organization 9
1.4.2 Manual Utilization 10

SECTION 2 PROCESS DESCRIPTION OVERVIEW 13

2.1 Coal Feed Characteristics and Product Slate 17
2.2 Base Plant Description 20
2.2.1 Coal Preparation 20
2.2.2 K-T Coal Gasification 21
2.2.3 Gas Purification and Upgrading 22
2.2.4 Product Synthesis 25
2.2.5 Auxiliaries 28
2.2.6 Fugitive and Miscellaneous Wastes 28
2.3 Base Plant Capital Investment and Annualized Operating Costs 30

SECTION 3 PROCESS DESCRIPTION AND WASTE STREAM CHARACTERIZATION . . 33

3.1 Coal Preparation 42
3.2 Coal Gasification 52
3.3 Gas Purification and Upgrading 60
3.3.1 Gas Cooling and Dust Removal 60
3.3.2 NO_x Reduction 69
3.3.3 Raw Gas Compression and Cooling 70
3.3.4 Cyanide Wash 74
3.3.5 Shift Conversion 78
3.3.6 Acid Gas Removal 83
3.3.7 Trace Sulfur Removal 89

CONTENTS (Continued)

3.4 Product Synthesis 91
3.4.1 Methanol Synthesis 92
3.4.2 Fischer-Tropsch (F-T) Synthesis 96
3.4.3 Methane Co-production (Fischer-Tropsch Synthesis Case) 98
3.4.4 Mobil M-gasoline Synthesis 100
3.4.5 Product Recovery and Upgrading 105
3.4.6 Waste Streams Generated by Synthesis Operations . 106
3.5 Products and By-Products 111
3.5.1 Methanol Synthesis Product 111
3.5.2 Fischer-Tropsch Liquid Products 113
3.5.3 Mobil M-gasoline Products 114
3.5.4 Substitute Natural Gas (SNG) 119
3.5.5 LP Gas 119
3.5.6 By-Product Sulfur (Stream 112) 119
3.6 Auxiliaries 121
3.6.1 Raw Water Treatment 121
3.6.2 Power Generation and Process Heating 128
3.6.3 Cooling Operations 134
3.6.4 Oxygen Production 137
3.6.5 Product and By-Product Storage 138
3.7 Fugitive and Miscellaneous Wastes 142
3.7.1 Fugitive Organic Emissions (Stream 241) 142
3.7.2 Non-Process/Intermittent Wastewater Streams . . . 143
3.7.3 Equipment Cleaning Wastes (Streams 242 and 305) . 146
3.8 Waste/Control Technology Index 147

SECTION 4 EVALUATION OF POLLUTION CONTROL TECHNOLOGY 163

4.1 Gaseous Medium 169
4.1.1 Acid Gases Containing Reduced Sulfur/Nitrogen, Organics, and/or Carbon Monoxide 173
4.1.2 Combustion Gases 218
4.1.3 Organic and CO Containing Waste Gases 249
4.1.4 Fugitive Dust from Material Storage (Stream 200) . 254
4.1.5 Fugitive VOC Emissions 259
4.1.6 Fugitive Particulates from Material Conveying and Processing 274
4.2 Aqueous Medium 276
4.2.1 Water Pollution Control Processes 285
4.2.2 Water Pollution Controls for Streams Containing Predominantly Organic Constituents 309
4.2.3 Water Pollution Controls for Streams Containing Predominantly Inorganic Constituents 320
4.2.4 Integrated Pollution Control Examples 335

CONTENTS (Continued)

4.3 Solid Waste Management 370
4.3.1 Solid Waste Control 375
4.3.2 Inorganic Ashes and Sludges 390
4.3.3 Recovered By-Products 404
4.3.4 Organic Sludges 405
4.3.5 Spent Catalysts and Sulfur Guard 408

SECTION 5 DATA GAPS AND LIMITATIONS 411

SECTION 6 REFERENCES 432

Appendix A Costing A-1
Appendix B Rectisol Acid Gas Removal Process B-1

FIGURES

Number Page

2-1 Simplified flow diagram for K-T based synthesis gas production 14

2-2 Simplified flow diagram for conversion of synthesis gas to liquids 15

3-1 Operations associated with synthesis gas production in K-T based indirect liquefaction facilities 34

3-2 Synthesis operations associated with K-T based indirect liquefaction facilities 35

3-3 Auxiliary processes associated with K-T based indirect liquefaction facilities 36

3-4 Waste streams associated with coal preparation for a K-T based indirect liquefaction facility - Illinois No. 6 coal 44

3-5 GKT's gasifier with waste heat boiler and slag extraction system 53

3-6 Gas cooling and dust removal 61

3-7 Raw gas compression and cooling 72

3-8 Shift conversion 82

3-9 Two-stage selective Rectisol acid gas removal system 85

3-10 Flow diagram for the ICI methanol synthesis process 93

3-11 Fischer-Tropsch (Synthol) synthesis and product recovery . . . 97

3-12 Methanation, CO_2 removal, and drying for SNG production . . . 101

3-13 Flow diagram for Mobil M-gasoline synthesis and crude product fractionation 102

3-14 Flow diagram for base plant raw water treatment system 124

4-1 Three stage Claus plant with split flow option 176

4-2 The Stretford process 179

4-3 Example 1 - Claus bulk sulfur removal with Beavon/Stretford tail gas treatment 205

4-4 Example 2 - Claus bulk sulfur removal with SCOT tail gas treatment and incineration 210

4-5 Example 3 - Claus bulk sulfur removal with Wellman-Lord tail gas treatment 214

FIGURES (Continued)

Number		Page
4-6	Integrated control examples - Mobil M or F-T synthesis case .	340
4-7	Integrated control examples for base plants producing crude methanol - discharge to surface waters	352
4-8	Integrated control examples for base plants producing crude methanol - discharge to surface impoundment or deep well injection	353
4-9	Landfill design	383
4-10	Capital investment and annualized unit cost for landfills . .	384
4-11	Surface impoundment design	387

TABLES

Number		Page
1-1	Completed and Ongoing Data Acquisition Programs at Coal Gasification Facilities Sponsored or Co-Sponsored by the EPA	8
2-1	Proximate and Ultimate Analyses of Base Plant Illinois No. 6 Coal	17
2-2	Estimated Product/By-Product Slate for K-T Base Plants . . .	19
2-3	Capital Costs for Uncontrolled K-T Based Indirect Liquefaction Plants	30
2-4	Annualized Costs for K-T Based Indirect Liquefaction Plants .	31
3-1	Flows of Major Streams for K-T Based Indirect Liquefaction Facilities - Illinois No. 6 Coal	38
3-2	Characteristics of Illinois No. 6 Coal Selected for Use in Indirect Liquefaction Base Plants	43
3-3	Coal Preparation Section Mass Flows - Methanol Synthesis Case	46
3-4	Estimated Fugitive Dust Emissions from Coal Storage Piles . .	47
3-5	Particulate Emissions from Coal Preparation (Illinois No. 6 Coal)	50
3-6	Material Flow Estimates for K-T Gasification (Illinois No. 6 Coal)	56
3-7	Results of K-T Slag Leaching Tests	57
3-8	Material Flow Estimates for Raw Gas Cooling and Dust Removal Processes (Illinois No. 6 Coal)	63
3-9	Leachability of Selected Elements from K-T Dust and from Illinois No. 6 Feed Coal	66
3-10	Characteristics of Blowdown from Cooling and Dust Removal . .	68
3-11	Material Flow Estimates for K-T NO_x Reduction, Compression and Cooling, and Cyanide Wash Processes (Illinois No. 6 Coal) . .	71
3-12	Characteristics of Primary Compression and Cooling Condensate from South African Sub-bituminous Coal	74
3-13	Material Flow Estimates for K-T Shift Conversion and Acid Gas Removal Processes (Illinois No. 6 Coal)	87
3-14	Methanol Synthesis Material Flow Estimates for K-T Gasification (Illinois No. 6 Coal)	95

TABLE (Continued)

Number		Page
3-15	Fischer-Tropsch Synthesis Material Flow Estimates for K-T Gasification (Illinois No. 6 Coal)	99
3-16	Mobil M-gasoline Synthesis Material Flow Estimates for K-T Gasification (illinois No. 6 Coal)	104
3-17	Components Reported in Commercial Methanol	112
3-18	Estimated Composition of Crude Methanol from Coal	113
3-19	Comparison of the Estimated Composition of Finished Indirect Coal Liquefaction, Unleaded Gasolines, and Typical Petroleum Gasolines	115
3-20	Distribution of Oxygenated By-Products from Fluid-Bed Fischer-Tropsch Synthesis	116
3-21	Methanol Conversion Unit Feed and Product Composition	117
3-22	Composition of Raw Makeup Water	122
3-23	Estimated Makeup Water Quantity for a K-T Based Indirect Liquefaction Plant (Illinois No. 6 Coal)	123
3-24	Raw Water Treatment Sludge (Stream 300) Production Rates and Characteristics	126
3-25	Demineralizer Regeneration Wastewater Composition (Stream 301)	127
3-26	Boiler Mass Flow for Illinois No. 6 Coal - Methanol Synthesis Case	130
3-28	Cooling System Makeup Water Requirements for a K-T Indirect Liquefaction Plant	135
3-29	Estimated Characteristics of Cooling Tower Blowdown and Drift	136
3-30	Evaporative Emission Estimates for Product and By-Product Storage	139
3-31	Composition of Evaporative Emissions from Gasoline Storage . .	141
3-32	Estimated Total Fugitive Organic Emissions	144
3-33	Drainage Estimate from Non-Process/Intermittent Streams . . .	145
3-34	Stream Index	148
3-35	Cross-Reference Index for Primary Waste Streams	154
3-36	Cross-Reference Index for Secondary Waste Streams	159

TABLE (Continued)

Number		Page
3-15	Fischer-Tropsch Synthesis Material Flow Estimates for K-T Gasification (Illinois No. 6 Coal)	99
3-16	Mobil M-gasoline Synthesis Material Flow Estimates for K-T Gasification (illinois No. 6 Coal)	104
3-17	Components Reported in Commercial Methanol	112
3-18	Estimated Composition of Crude Methanol from Coal	113
3-19	Comparison of the Estimated Composition of Finished Indirect Coal Liquefaction, Unleaded Gasolines, and Typical Petroleum Gasolines	115
3-20	Distribution of Oxygenated By-Products from Fluid-Bed Fischer-Tropsch Synthesis	116
3-21	Methanol Conversion Unit Feed and Product Composition	117
3-22	Composition of Raw Makeup Water	122
3-23	Estimated Makeup Water Quantity for a K-T Based Indirect Liquefaction Plant (Illinois No. 6 Coal)	123
3-24	Raw Water Treatment Sludge (Stream 300) Production Rates and Characteristics	126
3-25	Demineralizer Regeneration Wastewater Composition (Stream 301)	127
3-26	Boiler Mass Flow for Illinois No. 6 Coal - Methanol Synthesis Case	130
3-28	Cooling System Makeup Water Requirements for a K-T Indirect Liquefaction Plant	135
3-29	Estimated Characteristics of Cooling Tower Blowdown and Drift	136
3-30	Evaporative Emission Estimates for Product and By-Product Storage	139
3-31	Composition of Evaporative Emissions from Gasoline Storage . .	141
3-32	Estimated Total Fugitive Organic Emissions	144
3-33	Drainage Estimate from Non-Process/Intermittent Streams . . .	145
3-34	Stream Index	148
3-35	Cross-Reference Index for Primary Waste Streams	154
3-36	Cross-Reference Index for Secondary Waste Streams	159

TABLES (Continued)

Number | | Page
4-1 Summary of Estimated Gaseous Waste Stream Characteristics in K-T Based Indirect Liquefaction Facilities 170

4-2 Categorization of Gaseous Waste Streams According to Source Type in K-T Indirect Liquefaction Facilities 171

4-3 Key Features of Bulk Sulfur Removal Processes 175

4-4 Key Features of Residual Sulfur Removal Processes 183

4-5 Comparison of Incineration Processes 188

4-6 Example 1 - Material Flow Estimates for Integrated Control Employing Claus Bulk Sulfur Removal with Beavon/Stretford Tail Gas Treatment 206

4-7 Example 1 - Costs of Integrated Claus Bulk Sulfur Removal with Beavon/Stretford Tail Gas Treatment (1980 Basis) . . . 208

4-8 Example 2 - Material Flow Estimates for Integrated Control Employing Claus Bulk Sulfur Removal, SCOT Tail Gas Treatment, and Incineration 211

4-9 Example 2 - Costs of Integrated Claus Bulk Sulfur Removal with SCOT Tail Gas Treatment and Incineration (1980 Basis) . 213

4-10 Example 3 - Material Flow Estimates for Integrated Control Employing Claus Bulk Sulfur Removal with Wellman-Lord Tail Gas Treatment 215

4-11 Example 3 - Costs of Integrated Claus Bulk Sulfur Removal with Wellman-Lord Tail Gas Treatment (1980 Basis) 217

4-12 Combustion Modification Techniques for NO_x Control 221

4-13 NO_x Flue Gas Treatment Control Alternatives for Boilers . . 228

4-14 Key Features of Particulate Collection Equipment 234

4-15 Key Features of SO_2 Removal Processes 237

4-16 Composition of Flue Gas from the Dewatered Dust-Fired Fluidized-Bed Boiler (Stream 413) 246

4-17 Key Features of Storage Pile Dust Control Technologies . . . 255

4-18 Repair Methods for Fugitive Emissions Reduction 264

4-19 Equipment Design/Modifications for Fugitive Hydrocarbon Emissions Control 265

TABLES (Continued)

Number		Page
4-20	Storage Tank Emission Estimates	267
4-21	Estimated Incremental Costs for Storage of Synthetic Liquids	269
4-22	Fugitive Organic Emissions from Process Equipment	271
4-23	Capital and Annualized Costs for Fugitive Organic Emission Controls	273
4-24	Summary of K-T Base Plant Wastewater Streams and Estimated Characteristics	277
4-25	Categorization of Aqueous Waste Streams in K-T Gasification Facilities	280
4-26	Control Processes Potentially Applicable to the Treatment of K-T-Based Gasification Plant Wastewaters	286
4-27	Material Flow for Cooling Tower Concentration - Mobil M Synthesis Case	314
4-28	Material Flow for Forced Evaporation-Mobil M Synthesis Case	317
4-29	Material Flow for Cooling Tower Concentration and Forced Evaporation - Water-Based Cyanide Wash Case	326
4-30	Material Flow for Cooling Tower Concentration and Forced Evaporation - Methanol-Based Cyanide Wash Case	331
4-31	Characterization of Major Streams Combined for Common Treatment - Mobil M Synthesis Case	338
4-32	Example 1 - Material Flow for Mobil M Synthesis Base Plant Integrated Controls	342
4-33	Example 2 - Material Flow for Mobil M Synthesis Base Plant Integrated Controls	345
4-34	Example 3 - Material Flow for Mobil M Synthesis Base Plant Integrated Controls	347
4-35	Estimated Characteristics of Wastewater Streams Discharged to Ultimate Disposal - Mobil M Synthesis Case	348
4-36	Costs of Integrated Control Examples - Mobil M Synthesis Case	349
4-37	Characterization of Major Streams to be Combined for Treatment - Crude Methanol Production Case	355
4-38	Example 4 - Material Flow for Crude Methanol Production Base Plant Integrated Controls	357

TABLES (Continued)

Number		Page
4-39	Example 5 - Material Flow for Crude Methanol Production Base Plant Integrated Controls	358
4-40	Example 6 - Material Flow for Crude Methanol Production Base Plant Integrated Controls	363
4-41	Example 7 - Material Flow for Crude Methanol Production Base Plant Integrated Controls	364
4-42	Example 8 - Material Flow for Crude Methanol Production Base Plant Integrated Controls	365
4-43	Estimated Characteristics of Wastewater Streams Discharged to Ultimate Disposal - Crude Methanol Production Case	366
4-44	Costs of Integrated Control Examples - Crude Methanol Production Case	367
4-45	Summary of Solid Waste Streams from K-T-Based Indirect Liquefaction Facilities	371
4-46	Summary of Solid Waste Management Technologies	376
4-47	Site-Specific Factors to be Considered for Land-Based Disposal Options	377
4-48	Estimated Flow Rates for the Inorganic Ash and Sludge Streams	390
4-49	Characteristics of Flue Gas and Spent Bed Media from FBC Boiler	396
4-50	Estimated Capital Investment and Total Annualized Cost for Burning Dewatered Gasifier Dust in FBC Boiler	397
4-51	Summary of Capital Investment and Total Annualized Cost for Disposing of Gasifier Dust in Surface Impoundment	399
4-52	Estimated Treatment/Disposal Cost for Biosludge	406
4-53	Estimated Flow Rates for Spent Catalysts and Sulfur Guard . .	408
5-1	Completed and Ongoing Data Acquisition Programs at Coal Gasification Facilities Sponsored or Co-Sponsored by the EPA . .	415
5-2	Data Gaps and Research Needs - Gaseous Medium	416
5-3	Data Gaps and Research Needs - Aqueous Medium	422
5-4	Data Gaps and Research Needs - Solid Medium	438
5-5	Data Gaps and Research Needs - Products/By-Products	431

TABLES (Continued)

Number | Page

4-39 Example 5 - Material Flow for Crude Methanol Production Base Plant Integrated Controls . . . 358

4-40 Example 6 - Material Flow for Crude Methanol Production Base Plant Integrated Controls . . . 363

4-41 Example 7 - Material Flow for Crude Methanol Production Base Plant Integrated Controls . . . 364

4-42 Example 8 - Material Flow for Crude Methanol Production Base Plant Integrated Controls . . . 365

4-43 Estimated Characteristics of Wastewater Streams Discharged to Ultimate Disposal - Crude Methanol Production Case . . . 366

4-44 Costs of Integrated Control Examples - Crude Methanol Production Case . . . 367

4-45 Summary of Solid Waste Streams from K-T-Based Indirect Liquefaction Facilities . . . 371

4-46 Summary of Solid Waste Management Technologies . . . 376

4-47 Site-Specific Factors to be Considered for Land-Based Disposal Options . . . 377

4-48 Estimated Flow Rates for the Inorganic Ash and Sludge Streams . . . 390

4-49 Characteristics of Flue Gas and Spent Bed Media from FBC Boiler . . . 396

4-50 Estimated Capital Investment and Total Annualized Cost for Burning Dewatered Gasifier Dust in FBC Boiler . . . 397

4-51 Summary of Capital Investment and Total Annualized Cost for Disposing of Gasifier Dust in Surface Impoundment . . . 399

4-52 Estimated Treatment/Disposal Cost for Biosludge . . . 406

4-53 Estimated Flow Rates for Spent Catalysts and Sulfur Guard . . . 408

5-1 Completed and Ongoing Data Acquisition Programs at Coal Gasification Facilities Sponsored or Co-Sponsored by the EPA . . . 415

5-2 Data Gaps and Research Needs - Gaseous Medium . . . 416

5-3 Data Gaps and Research Needs - Aqueous Medium . . . 422

5-4 Data Gaps and Research Needs - Solid Medium . . . 438

5-5 Data Gaps and Research Needs - Products/By-Products . . . 431

GLOSSARY OF ACRONYMS

ACP	Ammonia from Coal Project
ADA	Anthraquinone disulfonic acid
ADIP	Shell-patented diisopropyl amine-based acid gas removal process
AGR	Acid gas removal
BM	Bureau of Mines
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CRA	Compression-refrigeration-absorption
CRF	Capital Recovery Factor
DEA	Diethanolamine
DIPA	Diisopropanolamine
DOE	Department of Energy
DOI	Department of Interior
EGD	Effluent Guidelines Division, Office of Water Regulations and Standards, EPA
EP	Extraction Procedure
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ERDA	Energy Research and Development Administration
ESP	Electrostatic precipitator
FGD	Flue gas desulfurization
FGR	Flue gas recirculation
FGT	Flue gas treatment
F-T	Fischer-Tropsch
GKT	Gesellschaft für Kohle-Technologie
HHV	Higher Heating Value
IERL	Industrial Environmental Research Laboratory
K-T	Koppers-Totzek
LEA	Low excess air
LHV	Lower Heating Value

GLOSSARY OF ACRONYMS (Continued)

LNB	Low NO_x burners
LPG	Liquified petroleum gas
MAF	Moisture and ash free
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
NFI	Nitrogenous Fertilizer Industry (S.A.)
NO_x	Nitrogen oxides
NMHC	Non-methane hydrocarbons
NPDES	National Pollutant Discharge Elimination System
NSPS	New Source Performance Standards
OAQPS	Office of Air QUality Planning and Standards, EPA
OFA	Overfire Air
OPTS	Office of Pesticides and Toxic Substances, EPA
OSW	Office of Solid Wastes, EPA
PCB	Polychlorinated Biphenyls
PCTM	Pollution Control Technical Manual
PNA	Polynuclear Aromatics
POM	Polycyclic organic matter
PSD	Prevention of Significant Deterioration
RCRA	Resource Conservation and Recovery Act
RL	Reduced Load
ROM	Run of Mine
SASOL	South African Coal, Oil and Gas Corporation, Ltd.
SCOT	Shell Claus Off-Gas Treatment
SCR	Selective Catalytic Reduction
SNG	Substitute Natural Gas
SNPA	Societe Nationale des Petroles d'Aquitaine
SO_x	Sulfur oxides
TDS	Total dissolved solids

GLOSSARY OF ACRONYMS (Continued)

TEA	Triethanolamine
TGT	Tail gas treatment
TOC	Total organic carbon
TSP	Total suspended particulates
TSS	Total suspended solids
TVA	Tennessee Valley Authority
VOC	Volatile Organic Compounds
W-L	Wellman-Lord

CONVERSION FACTORS

1.0 kg [kilogram] = 2.205 lb [pound (mass)]
1.0 Mg [megagram (metric ton)] = 1.102 ton [short ton (2000 lb)]
1.0 kg/min [kilogram per minute] = 132.3 lb/hr [pound per hour]
1.0 m^3 [cubic meter] = 264.2 gal [gallon]
1.0 Nm^3/hr [normal cubic meter (at 0°C) per hour] = 37.32 scfh [standard cubic feet (at 60°F) per hour]
1.0 GJ [gigajoule] = 0.9479 x 10^6 Btu [British thermal unit]
1.0 MW [megawatt] = 3.413 x 10^6 Btu/hr [British thermal unit per hour]
1.0 MJ/s [megajoule per second] = 3.413 x 10^6 Btu/hr [British thermal unit per hour]
1.0 kWh [kilowatt hour] = 3413 Btu [British thermal unit]
1.0 MJ/Nm^3 [megajoule per normal cubic meter (at 0°C)] = 25.40 Btu/scf [Btu per standard cubic foot (at 60°F)]
1.0 g/Nm^3 [gram per normal cubic meter (at 0°C)] = 0.413 gr/scf [grains per standard cubic foot (at 60°F)]
1.0 kPa [kilopascal] = 0.00987 atmosphere
1.0 kmole = 22.4 Nm^3 (at 0°C and 1 atmosphere)

Prefixes

T = tera = 10^{12} G = giga = 10^9 M = mega = 10^6 k = kilo = 10^3

ACKNOWLEDGEMENT

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SECTION 1

INTRODUCTION

Future U.S. energy production envisions the development of an environmentally acceptable synthetic fuels industry. As part of this overall effort, the Environmental Protection Agency (EPA), Office of Research and Development, has for the past several years undertaken extensive studies to determines synthetic fuel plant waste stream characteristics and potentially applicable pollution control systems.

The purpose of the Pollution Control Technical Manuals (PCTMs) is to convey in a summarized and readily useful manner, information on synfuel waste stream characteristics and pollution control technology as obtained from studies by EPA and others. The documents provide waste stream characterization data and describe a wide variety of pollution controls in terms of estimated performance, cost, and reliability. The PCTMs contain no legally binding requirements, no regulatory guidance, and include no preference for process technologies or controls. Nothing within these documents binds a facility to accepting the suggested emission control process(es) in the service(s) indicated nor relieves a facility from compliance with existing or future environmental regulations or permits.

The Pollution Control Technical Manuals consist of several discrete documents. There are six process-specific PCTMs and a more general appendix volume which describes over fifty pollution control technologies. Application of pollution controls to a particular synfuel process is described in each process specific manual. The volumes currently contemplated are:

Pollution Control Technical Manual for Lurgi-Based Indirect
Coal Liquefaction and SNG

Pollution Control Technical Manual for Koppers-Totzek-Based Indirect
Coal Liquefaction

Pollution Control Technical Manual for Exxon Donor-Solvent
Direct Coal Liquefaction

Section 1
Introduction

Pollution Control Technical Manual for Lurgi Oil Shale Retorting with Open Pit Mining

Pollution Control Technical Manual for Modified In-Situ Oil Shale Retorting Combined with Lurgi Surface Retorting

Pollution Control Technical Manual for TOSCO II Oil Shale Retorting with Underground Mining

Control Technology Appendices for the Pollution Control Technical Manuals

By focusing on specific process technologies, the PCTMs attempt to be as definitive as possible on waste stream characteristics and control technology applications. This focus does not imply any EPA recommendations for particular process or control designs. Those described in the manuals are intended as representative examples of processes and control technologies that might be used. The organization of the PCTMs from process description through waste stream characterization and control technology evaluation provides the user with a number of alternative approaches. Permit writers must be cautioned that these control technology configurations are not the only ones suitable for a specific plant.

Control technology configurations presented in the PCTMs reflect pollutant removal levels which are believed to be achievable with currently available control technologies based upon existing data. Since there are no domestic commercial scale synfuels facilities, the data base supporting this document is from bench and pilot synfuel facilities, developers' estimates, engineering analyses, analogue domestic industries, and non-U.S. commercial synfuel plants.

1.1 Koppers-Totzek Based Indirect Liqufaction

Indirect coal liquefaction links of two types of processes. One produces the H_2- and CO-rich synthesis gas from coal by gasification, while the second produces a range of synthetic liquid products by reacting the H_2 and CO components of a synthesis gas. A number of specific processes are available for the performance of both the gasification and synthesis steps. The combination of gasification and synthesis steps is in constrast with direct liquefaction, wherein any of several technologies can be used to directly produce liquid products from coal.

This PCTM addresses indirect liquefaction facilities for the production of synthetic fuels by means of Koppers-Totzek (K-T) coal gasification followed by any of three alternative fuel product synthesis routes, including methanol, Fischer-Tropsch, and Mobil M-gasoline. Facilities of this type utilize all of the process operations normally associated with indirect liquefaction, namely coal preparation; coal gasification and raw gas cleaning; shift conversion and acid gas removal; and synthesis of the desired fuel product. Auxiliary processes required to support these production operations are those required for oxygen production, raw water treatment, process cooling, and waste stream treatment. Depending upon the local availability and cost of electric power, on-site auxiliary power generation facilities may also be required.

The K-T process, as developed and licensed by Krupp-Koppers, GmbH, Essen, West Germany (Gesellschaft fur Kohle-Technologie (GKT) in the U.S.), is a commercially viable process which has been widely used outside the U.S. to produce industrial fuel gas and synthesis gas from coal. To date, the GKT K-T process has been used with a variety of coal feeds, ranging from brown coals through lignite and bituminous ranks and encompassing the full breadth of coking tendencies.

As a consequence of the recent formal separation of Koppers, Pittsburgh from Krupp-Koppers, a new gasifier has been designed and is being marketed by Koppers-Pittsburgh and Babcock and Wilcox as the KBW unit. While the KBW gasifier does incorporate different approaches (relative to K-T) to both heat recovery and dust separation, it does not appear to incorporate any features which would alter the actual gasification conditions, reactions or the extent of those reactions. Therefore, while the KBW gasifier has not been operated commercially and no specific process, operational or environmental data on the design were available for use in this manual, the Agency believes that the statements and examples presented herein regarding the K-T gasifier are also valid to a first approximation for the KBW gasifier.

All of the process operations discussions in this PCTM are largely based upon foreign experience, with the exception of the U.S.-developed Mobil M-gasoline process which is not yet in commercial operation. The methanol and Fischer-Tropsch synthesis processes have been commercially applied to the production of liquids from coal-derived synthesis gases. For purposes of this document, all of these technologies are considered ready for commercial application.

1.2 Approach to Manual Development

1.2.1 Base Plant Definition

In order to define the production operations and waste streams that would be associated with representative integrated process facilities, an uncontrolled base plant was defined which incorporates the features seen in the K-T-based plants which are either proposed, under construction, or currently in operation. In this context, an uncontrolled base plant is one which has full production capability (all of the equipment required to produce saleable produts) but no equipment to control pollutant discharges. Auxiliary processes included in the base plant are those that render a facility essentially self-sufficient in energy; i.e., one requiring only run-of-mine coal, raw water, and various chemicals and catalysts as inputs. Illinois No. 6 bituminous coal was examined as the primary feed to these facilities, with the impacts of using different ranks of coals with various heating values, moisture, sulfur, and ash contents being examined as variations to the primary coal. This approach permitted estimation of total stream and consistent flow rates in a process facility utilizing different feedstocks and served to define the range of uncontrolled (i.e., base plant) waste streams for which treatment and/or disposal could be considered.

A base plant size corresponding to approximately 120 TJ/day of clean synthesis gas produced was selected to be representative of the sizes of the modules of the first plants that may be built in the U.S. The energy output rate (after synthesis) of a plant of this size is equivalent to the energy content of about 20,000 bbls/day of gasoline. Using various data sources (discussed below), material flows and energy usages were estimated for all base plant feedstock/synthesis process combinations.

1.2.2 Control Technology Evaluation

The PCTMs examine control alternatives from three viewpoints: first, identifying several control technologies with their operating principles and applicability to particular types of waste streams and defining the inherent performance limitations of these control technologies; second, by using waste streams of given compositions as feeds to several of these control technologies, estimates of achievable control unit performance levels and costs are illustrated; and third, alternative integrated control trains are employed to treat base plant waste streams, thereby illustrating the range of overall control and control economics for individual streams. Each control technology utilized in the illustrative examples is further described in the control appendix volume.

Since very limited data on the performance of controls are available from operating synthetic fuels plants, many assumptions had to be made to extrapolate the experience gained with the same control technologies in related industries. These assumptions have been carefully documented in the appropriate sections of this manual. Waste streams resulting from pollution control process operations (secondary waste streams) were also identified and controls for those streams described and illustrated. Cost estimates for all controls were developed based upon published data and vendor-supplied estimates. These data were extrapolated to a 1980 cost basis to provide a consistent basis for comparing the relative costs of alternate controls. Base (uncontrolled) plant costs were extrapolated in a similar manner.

Users of this PCTM should recognize that there are two very significant limitations associated with the use of the data presented.

- First, no fully-integrated, well controlled commercial plants of the type discussed in this manual have been constructed to date. Thus, in using the data base presented here, users are cautioned to take careful note of the documented limitations in the data and assumptions made to resolve apparent differences in data obtained from test facilities having widely differing feedstocks, designs, operating characteristics, and site-specific constraints.
- Second, it should be noted that this manual does not attempt to address all of the issues that will be important in the selection and design of environmental control systems for new synthetic fuels facilities. Since this manual focuses on streams that tend to be unique to synfuels facilities, streams that are covered by existing source-based regulations or that are similar to waste streams routinely encountered in other industries for which regulatory precedents already exist are recognized but not treated in depth. Also, this PCTM focuses primarily on controls for point and fugitive sources of pollution, and not on the environmental impacts of those emissions.

  Fugitive dust from coal storage and handling facilities may have to be controlled to satisfy Prevention of Significant Deterioration (PSD) limitations associated with ambient particulate matter concentrations. Selecting appropriate controls for this type of emission requires more details on the use of technologies and site-specific analyses than are included in this manual.

  It should also be noted that this manual does not address issues related to worker health and safety, noise, socioeconomic, or ecological impacts.

1.3 Data Base

Since the early 1970's the EPA has sponsored a significant environmental assessment program addressing technologies for producing synthetic fuels from coal. This work has involved a combination of theoretical studies and plant data acquisition programs and has contributed to both the data and background knowledge used in the development of this document. Table 1-1 lists the major contributing data acquisition programs sponsored or co-sponsored by the EPA. As indicated, the data encompass specific research projects, pilot-level sampling and analysis projects, and source sampling of foreign and domestic commercial production facilities.

The major sources of data used to define the types and characteristics of uncontrolled synthetic fuels facility waste streams and to develop base plant/process configurations were: (1) an EPA-sponsored test program of a K-T gasification facility at Modderfontein, S.A.; (2) an EPA- and TVA-sponsored test program at the K-T facility at Ptolemais. Greece; (3) Linde/LOTEPRO research and EPA (IERL and OAQPS) sponsored tests at Rectisol installations; (4) DOE-sponsored gasoline-from-coal research studies conducted by Mobil Research and Development Corporation; and (5) permit filings, environmental impact statements, and design studies for various proposed K-T-based domestic synthetic fuel facilities. In addition, data derived from applications of controls in related industries such as the petroleum refining, natural gas processing, by-product coking, electric utility, and coal preparation industries were relied upon heavily in determining control applicability and costs.

Uncontrolled waste stream characteristics were estimated using overall material balance calculations and available compositional data from bench-, pilot-, and commercial-scale facilities based on similar technologies. The reader should recognize that K-T-based facilities built in the U.S. may contain design features that will result in different uncontrolled waste stream characteristics. Therefore, users of this manual should carefully consider the design features of a particular facility before making judgments concerning uncontrolled waste stream composition and the applicability and performance of candidate control technologies for these streams.

TABLE 1-1. COMPLETED AND ONGOING DATA ACQUISITION PROGRAMS AT COAL GASIFICATION FACILITIES SPONSORED OR CO-SPONSORED BY THE EPA

Facility	Information Classification	Coal Used	Products
Medium/High Btu Gasification and Indirect Liquefaction Facilities (Foreign)			
• Lurgi Gasification			
- Kosovo, Yugoslavia	Data acquisition	Lignite	Medium Btu gas
- SASOL, S.A.	Plant visit and discussions	Low rank bituminous	Various via indirect liquefaction
- Westfield, Scotland	Plant visit and discussions	Various	Test center
• Koppers-Totzek Gasification			
- Modderfontein, S.A.	Data acquisition	High volatile "B" bituminous	Ammonia, methanol
- Ptolemais, Greece	Data acquisition (TVA & EPA)	Ill. No. 6 bituminous	Ammonia
- Kutahya, Turkey	Plant visit and discussions	Lignite	Ammonia
• Winkler Gasification			
- Kutakya, Turkey	Plant visit and discussions	Lignite	Ammonia
• Texaco Gasification			
- Federal Republic of Germany	Data acquisition (EPRI, TVA & EPA)	Ill. No. 6 bituminous	Test center
Low-Btu Gasification Facilities (U.S.)			
• Wellman Galusha			
- Site No. 1	Data acquisition	Anthracite	Fuel gas
- Site No. 2	Data acquisition	Lignite	Test center
• Chapman/Wilputte	Data acquisition	Low sulfur bituminous	Fuel gas
• Riley	Data acquisition	Lignite	Test
• Stoic (Foster Wheeler)	Data acquisition (DOE & EPA)	Western bituminous	Fuel gas
Control Research Facilities			
• Raw/Acid Gas Cleanup (Fluidized Bed Gasifier)	North Carolina State Univ.	Various	Test center
• Wastewater Treatability Studies	Univ. of North Carolina	Various	Test center
• Pollutant Identification (Bench Scale Gasifier)	Research Triangle Institute	Various	Test center
• Ash Leaching Evaluations	University of Illinois	Various	Test center
Other Domestic Facilities			
• Texaco Gasification			
- Ammonia from coal plant, TVA	Data acquisition (TVA & EPA)	Ill. No. 6 bituminous (in shakedown)	Ammonia
• Rectisol Acid Gas Cleanup	Texaco, Wilmington, CA	Oil fired partial oxidation	Process hydrogen

1.4 Manual Organization and Utilization

1.4.1 Manual Organization

This Pollution Control Technology Manual is presented in two volumes. The main text volume describes the processes, their associated waste streams, and the pollutants potentially requiring control. It also provides descriptions and illustrative examples of pollution control technologies. Detailed information supporting the cost estimates cited in the main text can be found in the appendix of the main text volume. In addition, detailed discussions of control processes can be found in a separate appendix volume that is common to all PCTMs.

The subsequent sections of this volume provide:

Section 2	An overview of the process operations discussed in this manual.
Section 3	A description of the sources and characteristics of the waste streams generated by those process operations.
Section 4	An analysis of the performance capabilities and costs of candidate control processes for waste streams, including those generated by the control processes themselves.
Section 5	A summary of the quality of the data base used for the base plant development and control technology analysis.

Section 2 will be most useful to readers seeking a general knowledge of the characteristics of the gasification technology which this document addresses. Detailed information about the characteristics of specific uncontrolled waste streams is presented in Section 3. This section also describes how the characteristics of those streams are likely to be impacted by differences in feedstock (coal) characteristics, process design features, and plant operating characteristics. The rationale for the selection of specific control processes to serve as illustrative examples as well as an analysis of the expected performance of those controls is presented in Section 4. In light of the intended use of this document, this Section is most critical because it presents current estimates of the performance capabilities and costs of controls which have been or could be proposed for use in the subject facilities. Potential users of information presented in Section 4 should carefully note the data limitations summaries presented in Section 5 and should utilize the control appendices to establish the bases for adapting the PCTM base plant information to the specific case at hand. These summaries are intended to give potential users of this document a general feel for the quality of the data used to estimate both uncontrolled base plant waste stream characteristics and control equipment performance and cost data.

1.4.2 Manual Utilization

PCTM use has been targeted for those individuals concerned with the preparation of permits and the applications for them. As such, the interests of these plant designers and permit writers will focus both on grouped waste streams, with the common characteristics being the medium (i.e., air, water, or solid waste streams) and/or major pollutant species involved, as well as on individual streams which, because of their flow volume or constituents, could significantly impact environmental design criteria.

The PCTM accommodates these interests in several ways. First, the entire study is centered around a generalized uncontrolled "base" plant, which contains all of the production operations to be found in the coal conversion sections of K-T-based indirect liquefaction facilities; second, all waste streams (including control residuals or secondary wastes) are categorized by medium; and third, within each medium, the streams are grouped by major pollutant constituents.

To illustrate the utilization of the PCTM by someone with a designer's or permit writer's interest in a particular waste stream in a planned site-specific facility, the initial step will, of course, be to locate the counterpart waste stream in the base plant. This can be done through the use of the Section 2 and 3 flow diagrams and the stream and cross reference indicies in Section 3.8. Section 3 will provide both a full characterization of the counterpart base plant stream, plus a description of (as applicable) other base plant streams which may have to be analytically combined in order to better match the design stream in question.

Section 3.8 contains a process/waste stream index and cross reference indicies for waste streams. The process/waste stream index, Table 3-34, provides stream numbers for many process streams and all waste streams, and facilitates identification of streams discussed in the text. The cross reference index for primary waste streams, Table 3-35, lists: (1) all of the uncontrolled base plant waste streams and indicates the Section 3 subsection that contains detailed characterization data for each stream, and (2) the Section 4 subsection that contains information on potentially applicable pollution controls for each stream. The cross reference index for secondary waste streams, Table 3-36, provides similar information on the pollution controls discussed in Section 4, the secondary waste stream(s) generated by those controls, available controls for the secondary waste stream(s), and references to the appropriate Control Technology Appendices.

Should the user's interests lie only with waste stream controls, Table 3-35 will direct him to the appropriate level of discussion in Section 4. General control technology descriptions are followed by specific discussions of the performance, secondary waste streams, and costs associated with the application of example control techniques to specific waste streams. For example, Section 4.1.1.1 discusses the capabilities and costs of specific control processes applied to the offgases from the acid gas removal unit. Following the stream-by-stream discussions and examples of individual control applications are illustrative examples of potential integrated control schemes (i.e., multiple control techniques used in series) for those streams or combinations of streams which would normally be expected to use more than a single control (due to multiple pollutant loadings or other reasons). Similar types of information are presented for water pollution controls and solid waste management techniques in Sections 4.2 and 4.3, respectively. Additional "how to use" information is presented at the beginning of Sections 4.1, 4.2, and 4.3

If the user's interests involve a potential control residual or secondary waste stream, these and the location of applicable PCTM discussions of control alternatives can also be directly determined through the Table 3-36 cross reference index for secondary waste streams. The user will find that cross-media secondary wastes are generally discussed under the medium to which they contribute; exceptions are those peculiar cases in which the character of the secondary stream implies a potential for treatment in excess of that which would be provided if it were combined with other streams. In these cases, the control alternatives are discussed under the medium of origin.

Additional detail on the controls utilized in the Section 4 illustrative examples can be found in the Control Technology Appendices volume. Discussions of current commercial applications, performance, and the basis for both the performance and cost estimates are described there.

Limitations in the available data base are discussed in Section 5. The section is organized such that the data bases on both synfuel-unique primary streams and on the applicable control unit alternatives are covered. The user will find the counterpart base plant waste streams arranged by medium. This section covers the main base plant waste streams and associated secondary streams from potential control applications.

SECTION 2

PROCESS DESCRIPTION OVERVIEW

This section presents a brief description of the process operations and non-pollution control auxiliary processes expected to be included in Koppers-Totzek (K-T) based indirect liquefaction facilities. It also identifies the major uncontrolled waste streams associated with those operations and processes. The operations and processes described in this section comprise what is called an "uncontrolled base plant" or "base plant" since they are all required to produce marketable products and by-products. According to this definition, the "base plant" excludes those processes whose primary function is to treat waste streams to render them suitable for discharge or reuse within the plant. Base plant process operations discussed here include coal preparation, coal gasification, gas purification and upgrading, crude product synthesis and separation, and product upgrading. Auxiliary operations discussed include process cooling, product storage, raw water treatment, and oxygen production. Integrated K-T facilities are ordinarily more than self-sufficient with respect to process steam requirements. Further, on-site generation of electric power is not expected to be economical in the U.S. as compared with the purchase of power. However, on-site auxiliary power generation using coal as boiler fuel is examined in this document in an attempt to cover a broad range of possible plant configurations. Capital investment and operating costs for the base plant are also summarized.

Figure 2-1 presents a simplified block diagram of a K-T based synthesis gas production facility. The process operations associated with the synthesis of Fischer-Tropsch liquids, methanol, and gasoline-range hydrocarbons via the Mobil M process are shown in Figure 2-2. These base plant flow schemes are based upon published designs for existing facilities, and conceptual and proposed designs. They are believed to reasonably represent the

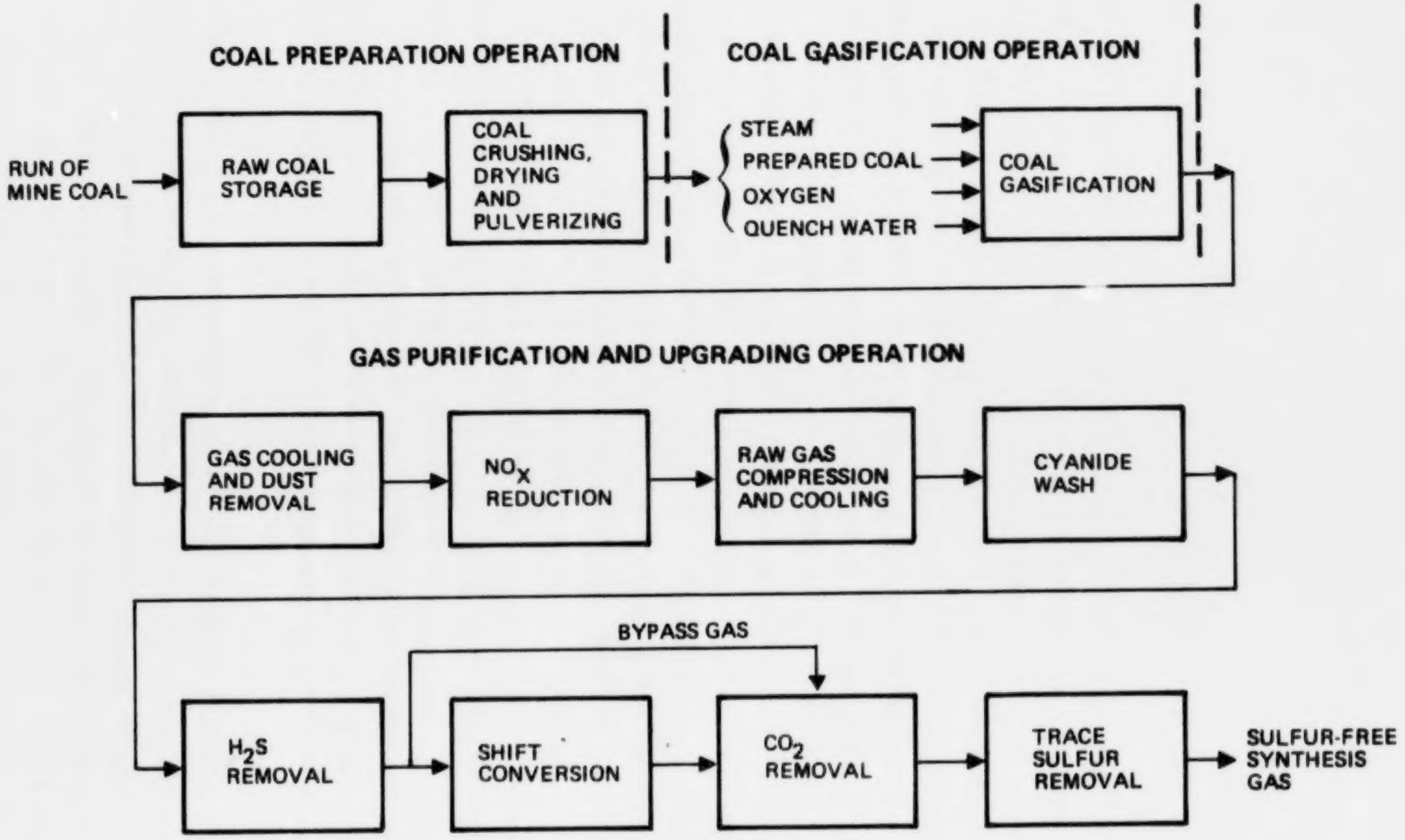
COAL PREPARATION OPERATION
COAL GASIFICATION OPERATION
RUN OF MINE COAL
RAW COAL STORAGE
COAL CRUSHING, DRYING AND PULVERIZING
STEAM
PREPARED COAL
OXYGEN
QUENCH WATER
COAL GASIFICATION
GAS PURIFICATION AND UPGRADING OPERATION
GAS COOLING AND DUST REMOVAL
NO_X REDUCTION
RAW GAS COMPRESSION AND COOLING
CYANIDE WASH
BYPASS GAS
H_2S REMOVAL
SHIFT CONVERSION
CO_2 REMOVAL
TRACE SULFUR REMOVAL
SULFUR-FREE SYNTHESIS GAS

Figure 2-1. Simplified flow diagram for K-T based synthesis gas production

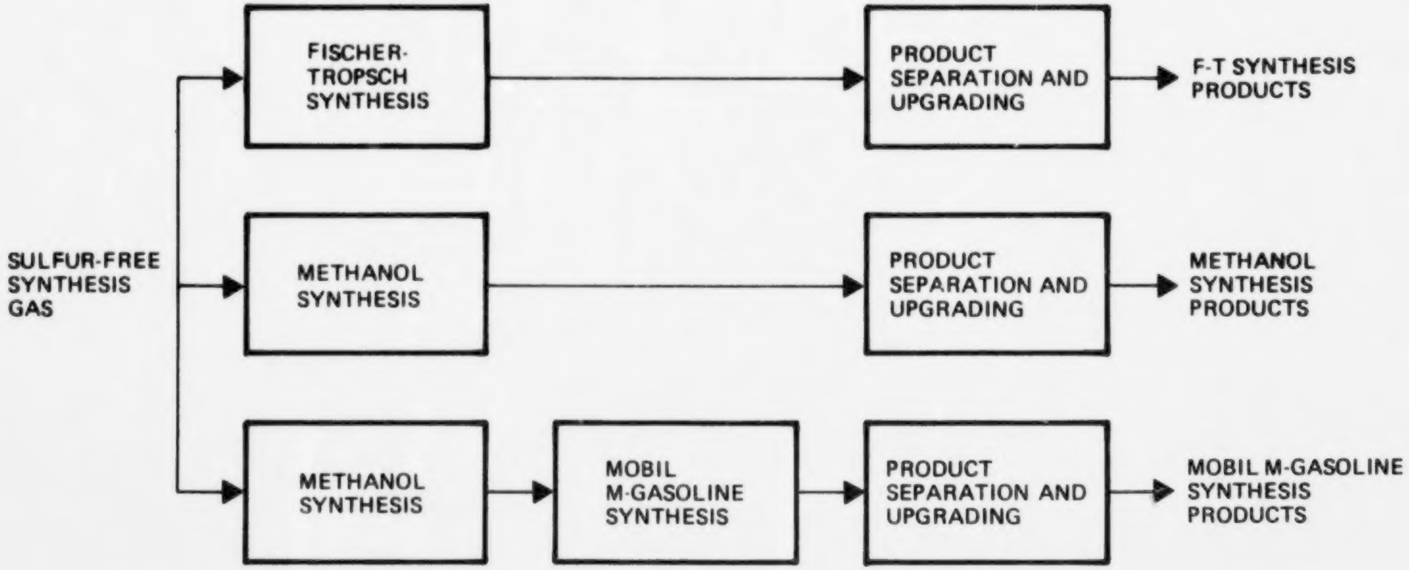
SULFUR-FREE SYNTHESIS GAS
FISCHER-TROPSCH SYNTHESIS
PRODUCT SEPARATION AND UPGRADING
F-T SYNTHESIS PRODUCTS
METHANOL SYNTHESIS
PRODUCT SEPARATION AND UPGRADING
METHANOL SYNTHESIS PRODUCTS
METHANOL SYNTHESIS
MOBIL M-GASOLINE SYNTHESIS
PRODUCT SEPARATION AND UPGRADING
MOBIL M-GASOLINE SYNTHESIS PRODUCTS

Figure 2-2. Simplified flow diagram for conversion of synthesis gas to liquids

configuration options that are likely to be incorporated into the first generation facilities built in the U.S.

2.1 COAL FEED CHARACTERISTICS AND PRODUCT SLATE

A wide variety of domestic coals are potential feedstocks for K-T based synthetic fuels facilities. In general, specific characteristics of the coal feedstocks will determine the characteristics of process and waste streams. To date, the North Alabama Coal Gasification Consortium has performed large scale K-T gasification tests only with an Illinois No. 6 coal. Thus, an Illinois No. 6 coal was chosen for examination in this PCTM to provide a basis for sizing and characterizing base plant process and waste streams and evaluating waste stream control options and costs. Characteristics of the base plant Illinois No. 6 coal are summarized in Table 2-1. The effects of differing feed coal characteristics, particularly with respect to waste stream generation rates and characteristics, are discussed qualitatively and, to an extent consistent with available data, quantitatively in Section 3.

TABLE 2-1. PROXIMATE AND ULTIMATE ANALYSES OF BASE PLANT ILLINOIS NO. 6 COAL

Analyses	Composition
Proximate Analysis, wt %	
Moisture	10.2
Volatile matter	34.7
Fixed carbon	46.0
Ash	9.1
Higher Heating Value, MJ/kg (as received)	26.6
Ultimate Analysis, wt % (dry basis)	
Carbon	71.5
Hydrogen	4.8
Nitrogen	1.4
Sulfur	3.1
Chloride	0.28
Ash	10.1
Oxygen (by difference)	9.0

In developing the base plant material flow estimates, a fixed coal feed rate of 6682 Mg per day (dry basis) to gasification corresponding to 120 TJ/day synthesis gas was used. In addition to the gasifier coal requirements, some K-T based synfuels facilities may include on-site coal-fired auxiliary boilers for power generation. Coal requirements for any such boilers will depend upon the amount of purchased electricity from off-site sources. Boiler fuel requirements could also be offset by using high energy process waste gases as fuel. Due to the large number of variables that affect the auxiliary boiler coal requirements, it is difficult to estimate the quantity of or need for boiler feed coal for each type of synfuels plant examined in this manual. For facilities which are self-sufficient in energy, auxiliary boiler energy requirements for electric power are expected to range from about 4 to 26% of the coal energy input to the gasifier. It should be noted that most plants are potentially self-sufficient with respect to steam and, depending upon the cost of electric power, an on-site power boiler may not be needed at all.

Typical upgraded product slates for the K-T based synfuels plants examined in this PCTM are summarized in Table 2-2. As indicated in this table, the quantity and energy content of the products from each type plant varies even though the same quantity of synthesis gas is assumed in all cases (i.e., the same coal feed rate to gasification for all cases). This is a reflection of the different energy conversion efficiencies associated with the three different synthesis operations examined. The only K-T based indirect liquefaction facility proposed in the U.S. (The North Alabama Coal Gasification Consortium Project) is currently designed for methanol production.

TABLE 2-2. ESTIMATED PRODUCT/BY-PRODUCT SLATE FOR K-T BASED PLANTS*

Product/ By-Products	Methanol Synthesis		Mobil M-Gasoline Synthesis		Fischer-Tropsch Synthesis	
	Mg/day	TJ/day	Mg/day	TJ/day	Mg/day	TJ/day
Gasoline			1750	81.0	992	46.9
Diesel Oil					201	9.45
Fuel Oil					58.9	2.71
LPG			236	11.7	74.6	3.72
SNG					798	34.8
Alcohols	4710	113			171	5.38
Sulfur	202		202		202	
Total	4910	113	2190	92.7	2497	103.0

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*Coal feed rate to gasification is 6682 Mg per day (dry basis) which corresponds to 120 TJ/day of synthesis gas.

2.2 BASE PLANT DESCRIPTION

Base plant process operations consist of coal preparation, coal gasification, gas purification and upgrading, crude product synthesis and separation, and product upgrading. In addition, the auxiliary processes required to support a fully integrated, self-sufficient, liquid fuels production facility would include raw water treatment, power generation, and oxygen production. These processes and their associated waste streams are described briefly in this section. Detailed descriptions are presented in Section 3.

2.2.1 Coal Preparation

The coal preparation operation in a K-T based synfuels facility will be similar to those found in other coal-based plants such as pulverized coal-fired power plants. Equipment is provided to receive, transport, and store coal, and to prepare pulverized coal for gasification and consumption in on-site power boilers. Coal is received by conveyor, train, barge, or truck and is stored in either an active or inactive (emergency) storage pile, as necessary. Coal from storage is prepared for gasification/combustion by screening, crushing, drying, and pulverizing to a size predominantly less than 0.1 mm. Prepared coal moisture contents of 1 to 2% are required for gasification of bituminous coals and 8 to 10% are required for gasification of lignites. Dried and sized coal is stored in silos and transported to gasifiers and boilers as required.

Major waste streams associated with the coal preparation operation are storage pile runoff; fugitive dust emissions from coal storage and transport; and dust from coal screening, crushing, and pulverizing. Storage runoff tends to contain high levels of suspended and dissolved solids and can be quite acidic in the case of Midwestern and Eastern coals. Dust from coal preparation consists of natural soil and overburden material as well as coal.

2.2.2 K-T Coal Gasification

The K-T process involves low pressure (slightly above atmospheric), entrained-flow slagging coal gasification in the presence of steam and oxygen. Flame temperatures may range from 2000-2300K during gasification with reactor temperatures of 1510-1860K. The gasifier is a water-cooled steel vessel with a refractory lining, which, in the most common two-headed configuration, resembles an ellipsoid with horizontally opposing burners at the apices. The newest installations (three gasifiers each at Ramagundam and Talcher, India) employ four-headed gasifiers which resemble two intersecting ellipsoids with burners located 90 degrees apart at each of the four apices. Coal is introduced continuously into the gasifier through screw feeders at the burner heads and then entrained in a stream of low pressure steam and high purity oxygen. Partial oxidation reactions occur rapidly within the central portion of the gasifier; coal residence time is less than a second. Raw product gas and entrained dust exit the gasifier vertically upward through a waste heat boiler system producing high pressure saturated steam. Molten slag exits the bottom of the gasifier and falls into a quench tank where circulating cooling water causes it to shatter into granular form. Slag is removed from the quench tank by a drag chain conveyor on which dewatering occurs prior to subsequent slag disposal.

Waste streams associated with the gasification operation are quenched slag and transient waste gases. K-T slag is a coarse, pebble sized material which is physically stable and essentially inert. Quenched slag has about the same composition as the parent coal ash and retains about 10% moisture. Depending upon the quench water quality, and whether the slag is rinsed, contaminants such as NH_4^+ and SCN^- may be present in the slag moisture. Transient gases unsuitable for processing into synthetic liquids may be generated for short periods of time (less than 1/2 hour) during startup, shutdown, and unscheduled transient operations. These waste gases will vary in composition but are similar to either gases from heavy oil combustion or raw K-T product gas depending upon the gasifier conditions during the particular transient period.

2.2.3 Gas Purification and Upgrading

The gas purification and upgrading operation consists of (1) gas cooling and dust removal; (2) NO_x reduction; (3) raw gas compression and cooling; (4) cyanide washing; (5) shift conversion; (6) acid gas removal; and (7) trace sulfur removal.

Gas Cooling and Dust Removal

Hot raw gas from the waste heat boiler is cooled and scrubbed of entrained dust in two stages by means of direct water contacting. Final dedusting is provided by a wet electrostatic precipitator. The collected dust slurry is pumped to settling basins for thickening. Most of the clear water overflowing the settlers is indirectly cooled and recycled. The settler underflow is filtered to produce dewatered dust (up to 50% moisture) and filtrate which is combined with a portion of the clarifier overflow as blowdown for controlling the buildup of dissolved components within the washer system.

Waste streams associated with the gas cooling and dust removal process are dewatered dust and blowdown. Gasification dust consists primarily of coal ash and unreacted carbon. The dust is combustible and has leachable components. In addition, moisture associated with the dust will be similar in composition to the washer blowdown, containing contaminants such as NH_4^+, CN^-, SCN^-, $S_2O_3^=$, $SO_4^=$, Cl^-, and other species.

NO_x Reduction

The NO_x reduction unit catalytically hydrogenates nitrogen oxides and oxygen present in the raw synthesis gas to eliminate associated fouling on compressor blades and in the acid gas removal system. Although such a unit is currently in use at an operating K-T based facility, details regarding unit performance and reaction chemistry are not available. The only waste stream expected from this unit is spent cobalt molybdate catalyst which will periodically require disposal.

Raw Gas Compression and Cooling

Koppers-Totzek technology involves coal gasification at essentially atmospheric pressure. However, downstream operations such as cyanide wash, shift conversion, acid gas removal, and liquid product synthesis are more efficient and economical at elevated pressures. Therefore, raw gas from cooling and dust removal is compressed to about 3 MPa prior to subsequent treatment. The temperature rise of the gas during compression is controlled by intercoolers and an aftercooler, consistent with materials limitations and temperature requirements of downstream processes.

The principal waste stream from raw gas compression and cooling is compression condensate. Contaminants expected to be present in the condensate include NH_4^+, Cl^-, $S^=$, SCN^-, and CN^-.

Cyanide Wash

Hydrogen cyanide and any residual ammonia present in the raw synthesis gas are removed by absorption in either water or cold methanol. In the case of a water-based cyanide wash, rich wash water from the absorber is flashed to atmospheric pressure yielding depressurized wash water and a sour flash gas. In the case of a methanol-based cyanide wash, rich methanol from the absorber is regenerated by depressurization and indirect heating to also yield a sour flash gas. Water vapor coabsorbed with the cyanide is recovered from the process methanol by distillation.

Major waste streams associated with a water-based cyanide wash process are depressurized wash water and sour flash gas. Depressurized wash water is expected to contain CN^-, $S^=$, and traces of NH_4^+. Sour flash gas from a water-based cyanide wash is expected to consist primarily of CO_2 and H_2S

with lower levels of HCN. The major waste stream associated with a methanol-based cyanide wash process is sour flash gas. Sour flash gas from a methanol-based cyanide wash is expected to consist primarily of H_2S, CO, HCN, CO_2, COS, H_2, and methanol vapor.

Shift Conversion

Gases suitable for feed to methanol synthesis or hydrocarbon production via Fischer-Tropsch synthesis should have somewhat greater than a 2:1 ratio of H_2 to CO and no more than a few percent CO_2. The H_2 to CO ratio in raw K-T gas typically ranges from 1:2 to 1:2.5, well below the ratio required for liquids synthesis. Thus, a shift conversion step is a necessary part of the gas upgrading. All commercial scale K-T based coal gasification facilities employ a shift conversion unit which follows raw gas sulfur removal and precedes CO_2 removal, and this approach has been incorporated into the base plant design. This approach enables the use of conventional iron-chromium or copper-zinc shift catalysts. Also, due to the favorable H_2S to CO_2 ratio before shift conversion, it facilitates production of an H_2S-rich offgas for economic sulfur recovery.

Waste streams produced by shift conversion are spent shift catalyst which periodically requires replacement and shift condensate blowdown which is expected to be reused as makeup water to the gasification quench circuit.

Acid Gas Removal

Removal of H_2S and other sulfur compounds present in the raw K-T gas is necessary to prevent catalyst poisoning in subsequent shift conversion, and methanol and Fischer-Tropsch synthesis operations. Bulk removal of CO_2 is necessary to obtain a composition meeting the stoichiometric requirements for synthesis feed gas. There are several acid gas removal processes which have been demonstrated in coal gasification or similar applications. However, only the two-stage selective Rectisol process has been included in the base plant design, since all commercial scale K-T based coal gasification facilitates utilize two-stage selective Rectisol units and the only K-T based indirect liquefaction facility proposed in the U.S. (The North Alabama Coal Gasification Consortium Project) is also expected to use this process.

Rectisol is a physical absorption process using low temperature methanol as a solvent. In two-stage selective Rectisol systems, sulfur compounds are removed from the raw gas prior to shift conversion and subsequent CO_2 removal. This facilitates high process selectivity due to the favorable H_2S to CO_2 ratio before shift conversion. Sulfur laden methanol from sulfide absorption is enriched by flashing and stripping a portion of the absorbed CO_2 and then regenerated in a hot stripper to produce a sulfur-rich offgas typically containing 25 to 35% H_2S. Carbon dioxide laden methanol from the CO_2 absorber is regenerated by flashing and stripping with N_2 to produce a CO_2-rich offgas. An additional waste stream from the Rectisol system is still bottoms from a methanol/water distillation unit which controls moisture buildup in the methanol solvent.

Trace Sulfur Removal

To protect synthesis catalysts from sulfur poisoning, zinc oxide guard beds may be used following the Rectisol process to remove residual traces of sulfur compounds. Ordinarily the Rectisol process can attain levels of less than 0.1 ppmv total sulfur species in the synthesis feed gas, but ZnO provides for temporary removal during periods of Rectisol process upsets. Periodically, sulfur guard material must be decommissioned and replaced. This generates a solid waste consisting of spent ZnO/ZnS.

2.2.4 Product Synthesis

Methanol synthesis and hydrocarbon production via Fischer-Tropsch (F-T) synthesis can be represented by the following reaction:

$$CO + 2H_2 \rightarrow CH_3OH + \text{heat (Methanol Synthesis)}$$

$$nCO + (2n + 0.5x)\ H_2 \rightarrow C_nH_{2n+x} + nH_2O + \text{heat (F-T Synthesis)}$$

where n ranges from 1 to about 20, x = 2 for paraffins and x = 0 for olefins. The mix of F-T products obtained (i.e., the range of n and x values) is dependent upon several factors including the reactor design, temperature, pressure, and type of catalyst used. Synthesis gas usually contains some CO_2 in addition to CO and H_2. Because synthesis catalysts are also active for the hydrogenation of CO_2, the presence of CO_2 does not create problems as long as the synthesis gas contains the proper ratio of $H_2/(CO + CO_2)$. Methanol synthesis employs Cu/Zn-based catalysts at 470K and 3.5 to 7.0 MPa while F-T synthesis proceeds over iron-based catalysts at 600K and 2.3 MPa (fluidized bed reactors) or 500K and 2.7 MPa (fixed bed reactors).

Mobil M-gasoline synthesis from methanol can be represented as follows:

$$nCH_3OH \rightarrow (CH_2)_n + nH_2O \text{ (Mobil M-gasoline Synthesis)}$$

This process employs zeolite-based catalysts and operates at about 570K and 2.2 MPa.

The crude liquid fuel products of methanol, F-T, and Mobil M-gasoline synthesis processes will require upgrading (probably onsite) to yield final products which are marketable as substitutes for petroleum-derived fuels. This is particularly true for motor gasolines, where crude coal-derived gasoline fractions would not meet octane requirements for the retain market in the U.S. F-T and Mobil M-gasoline products could be upgraded by catalytic alkylation of the C_3-C_4 fraction to yield gasoline-blend hydrocarbons and commercial grade LPG by hydrotreating (in the F-T case) for destruction of olefins and oxygenated organics, by catalytic reforming to produce more cyclic and branched chain hydrocarbons, by C_5/C_6 isomerization to increase the anti-knock quality of pentanes and hexanes, and by catalytic polymerization to convert propene/butene fractions into higher molecular weight gasoline blending compounds. All of these upgrading processes will utilize conventional petroleum refinery technology. Since the feed streams to these upgrading processes in an indirect liquefaction plant are not expected to have any unusual characteristics relative to current refinery experience, waste streams generated during these upgrading operations are not expected to present any unique treatment problems. For these reasons and due to the multiplicity of possible options for product upgrading, waste stream characteristics and pollution control alternatives for product upgrading processes are not specifically discussed in this PCTM.

All of the synthetic liquid fuels synthesis processes generate a purge gas containing compounds such as unreacted carbon oxides, hydrogen, methane, and methanol. Several options are available to handle the purge gas including use as an on-site fuel, reforming to generate additional synthesis gas, or conversion of the residual hydrogen and carbon oxides into methane to produce SNG. Because supplemental fuel may be required for power generation in all synthesis cases, use of these purge gases as an on-site fuel was selected for analysis purposes in this PCTM. In actual practice, the decision regarding the disposition of synthesis purge gases involves site- and design-specific considerations which are outside the scope of this manual.

A variety of waste streams are associated with liquid product synthesis processes, exclusive of upgrading processes. Major waste streams from F-T synthesis include spent F-T and methanation catalysts, methanation catalyst decommissioning offgases, SNG dehydration offgases, carbon dioxide offgases, condensates, and wastewaters. Major waste streams from methanol synthesis include spent catalyst and synthesis condensate. Major waste streams from Mobil M-gasoline synthesis include spent methanol and Mobil catalysts, Mobil catalyst regeneration offgases, and wastewater.

2.2.5 Auxiliaries

The major additional auxiliary processing units required for self-sufficient K-T based synfuels facilities are: (1) on-site boiler for power generation; (2) makeup water treatment facilities; (3) process cooling water system; (4) liquid product/by-product storage facilities; and (5) oxygen production unit.

The most significant potential source of waste streams from the auxiliary processes is the boiler. The boiler flue gases are particularly important because the boilers will generally be coal-fired and are therefore potentially major sources of SO_x, NO_x, and particulate emissions. In addition to flue gases, waste streams resulting from the boilers include blowdown condensates and bottom ashes. It should be again noted that most plants are potentially self-sufficient with respect to steam and, depending upon the local availability and cost of electric power, an on-site power boiler may not be needed.

The major waste streams from makeup water treatment are sedimentation pond sludges, lime/soda softener sludges, and demineralizer regeneration wastewaters from the boiler feedwater treatment unit. Evaporated volatiles, drift, and cooling tower blowdown are the major waste streams from the cooling water system. Evaporative emissions are the major waste streams from product/by-product storage facilities.

2.2.6 Fugitive and Miscellaneous Wastes

In addition to the waste streams associated with specific processes, there are three general categories of wastes which are of non-specific origin. These categories are fugitive organic emissions, non-process/intermittent wastewater streams, and equipment cleaning wastes. There are many potential sources of fugitive organic emissions in an indirect coal liquefaction plant. These include pumps, compressors, valves, flanges, and pressure relief devices. Non-process waste streams include fluid leaks from sources such as pump seals, valves, and flanges. In addition, drainage resulting from emergency process fluid discharges or process area washdown/cleanup activities will contribute additional intermittent aqueous wastes. The two primary sources of equipment cleaning wastes in an indirect liquefaction facility are process equipment and boiler cleaning wastes.

2.3 BASE PLANT CAPITAL INVESTMENT AND ANNUALIZED OPERATING COSTS

In order to assess the relative impact of the costs of pollution controls on the total plant cost, approximate costs for uncontrolled base plants were developed. Both capital and operating costs for K-T plants were estimated and are presented in Tables 2-3 and 2-4, respectively. Details of the costing methodology are presented in Appendix A. These base plant cost estimates are used subsequently in Section 4 to evaluate the relative magnitude of costs for individual pollution control technologies; however, since control systems for an integrated facility are not evaluated in this manual, the total relative cost impact of pollution control has not been evaluated.

TABLE 2-3. CAPITAL COSTS FOR UNCONTROLLED K-T BASED INDIRECT LIQUEFACTION PLANTS*

Item	Capital Costs, 10^6 Dollars (1980 Basis) Methanol	Fischer-Tropsch	Mobil M-Gasoline
Installed cost	603	714	657
Contractors Overhead and Fee	18	21	20
Engineering and Construction	151	178	164
Contingency	121	143	131
Subtotal, Facility Cost	893	1056	972
Interest during Construction	201	238	220
Working Capital	17	20	17
Total Capital Investment	1111	1314	1209

*Capital cost estimates are based upon estimates published in references 1, 2, 3, 4, 5, and 6. Published estimates were scaled to a plant capacity of 6682 Mg dry coal per day to gasification. To the extent that they could be identified, capital costs associated with pollution controls were deleted from published cost estimates. Details of the costing methodology are presented in Appendix A.

TABLE 2-4. ANNUALIZED COSTS FOR K-T BASED INDIRECT LIQUEFACTION PLANTS*

	Annualized Cost, 10^6 Dollars		
	Methanol	Fischer-Tropsch	Mobil M-Gasoline
Coal	98	114	95
Water, Catalyst, and Chemicals*	4	4	4
Other Operating Costs*	53	63	51
Total Operating Cost	155	181	150
Capital Charges	191	226	208
Total Annualized Cost	346	407	358

*Annual operating costs relating to "water, catalyst, and chemicals" and "other operating costs" are based upon published cost estimates for a K-T based methanol production facility (3). Published estimates were scaled directly to a plant capacity of 6682 Mg dry coal per day to gasification. Insufficient details were available to enable adjustment, if any is required, for F-T and Mobil M-gasoline synthesis cases or to deduct the annual operating costs for pollution controls. Details of the costing methodology are presented in Appendix A.

Installed costs are based upon published cost estimates for K-T based methanol and hydrogen production facilities (3,4). Published cost data were adjusted to reflect differences in costs for methanol, F-T, and Mobil M-gasoline synthesis processes (1,2,3,5,6). To the extent that pollution control costs could be quantified, they were deleted from published installed costs. The resulting installed cost estimates were then scaled to the base plant capacity using a scaling exponent of 0.8. For analysis purposes, the adjusted base plant installed costs were escalated to 1980 dollars using the Chemical Engineering (CE) plant cost index. Total uncontrolled base plant capital investments were estimated to be \$1.1, \$1.3, and \$1.2 billion (1980 basis) for the methanol, F-T, and Mobil M-gasoline synthesis cases, respectively. Differences among the estimated capital investment costs derive primarily from differences in costs of the synthesis operation and, to a lesser extent, differences in on-site boiler costs.

The total operating costs are based upon the annual coal cost and published cost estimates for "water, catalyst, and chemicals" and "other operating costs" in a K-T based methanol production facility (3). Published operating cost estimates were scaled directly on the basis of plant capacity and escalated to 1980 dollars. Published cost estimates for "water, catalyst, and chemicals" and "other operating costs" relate specifically to a methanol production facility; however, no adjustment has been made for F-T and Mobil M-gasoline synthesis cases, if any is required, since insufficient details of these estimates are available to do so. Similarly, the annual operating costs of pollution control equipment have not been deducted from cost estimates for "water, catalyst, and chemicals" and "other operating costs" since insufficient details of these estimates are available to do so.

It should be noted that annual coal costs and annualized capital charges comprise about 84% of the total annualized cost. Therefore, uncertainties associated with estimated costs for "water, catalyst, and chemicals" and "other operating costs" are not expected to have a major impact on the estimated total annualized cost. Total annualized costs were estimated to be \$346, \$407, and \$358 million for the methanol, F-T, and Mobil M-gasoline synthesis cases, respectively.

SECTION 3

PROCESS DESCRIPTION AND WASTE STREAM CHARACTERIZATION

This section defines the basic operations and auxiliary processes associated with Koppers-Totzek (K-T) based indirect liquefaction facilities, and the characteristics of major associated process and waste streams. Material flow estimates are also presented to provide pertinent information relating to the magnitudes of the various waste streams and their environmental control needs. Operations covered by this manual are shown schematically in Figures 3-1 and 3-2. These operations include coal preparation, coal gasification, gas purification and upgrading, crude product synthesis and separation, and product upgrading. Auxiliary processes are shown in Figure 3-3 and include all of the operations which may be required to support a fully integrated, self-sufficient, liquid fuels production facility. These processes include raw water treatment, oxygen production, and product storage. Integrated K-T facilities are ordinarily more than self-sufficient with respect to steam requirements. Also, on-site power generation is not expected to be economical in the U.S. as compared with the purchase of power. However, on-site power generation using coal as boiler fuel is examined in this document in an attempt to cover a broad range of possible plant configurations. Stream numbers have been provided in the figures for major process streams and all waste streams to clarify stream identification in subsequent sections. A stream identification listing and cross referencing indicies are provided in Section 3.8. Figures 3-1 through 3-3 are based primarily upon published designs for existing facilities (e.g., the AECI Limited facility at Modderfontein, Republic of South Africa) and conceptual and proposed designs (e.g., the North Alabama Coal Gasification Consortium Project). They are believed to reasonably represent the configuration options that are likely

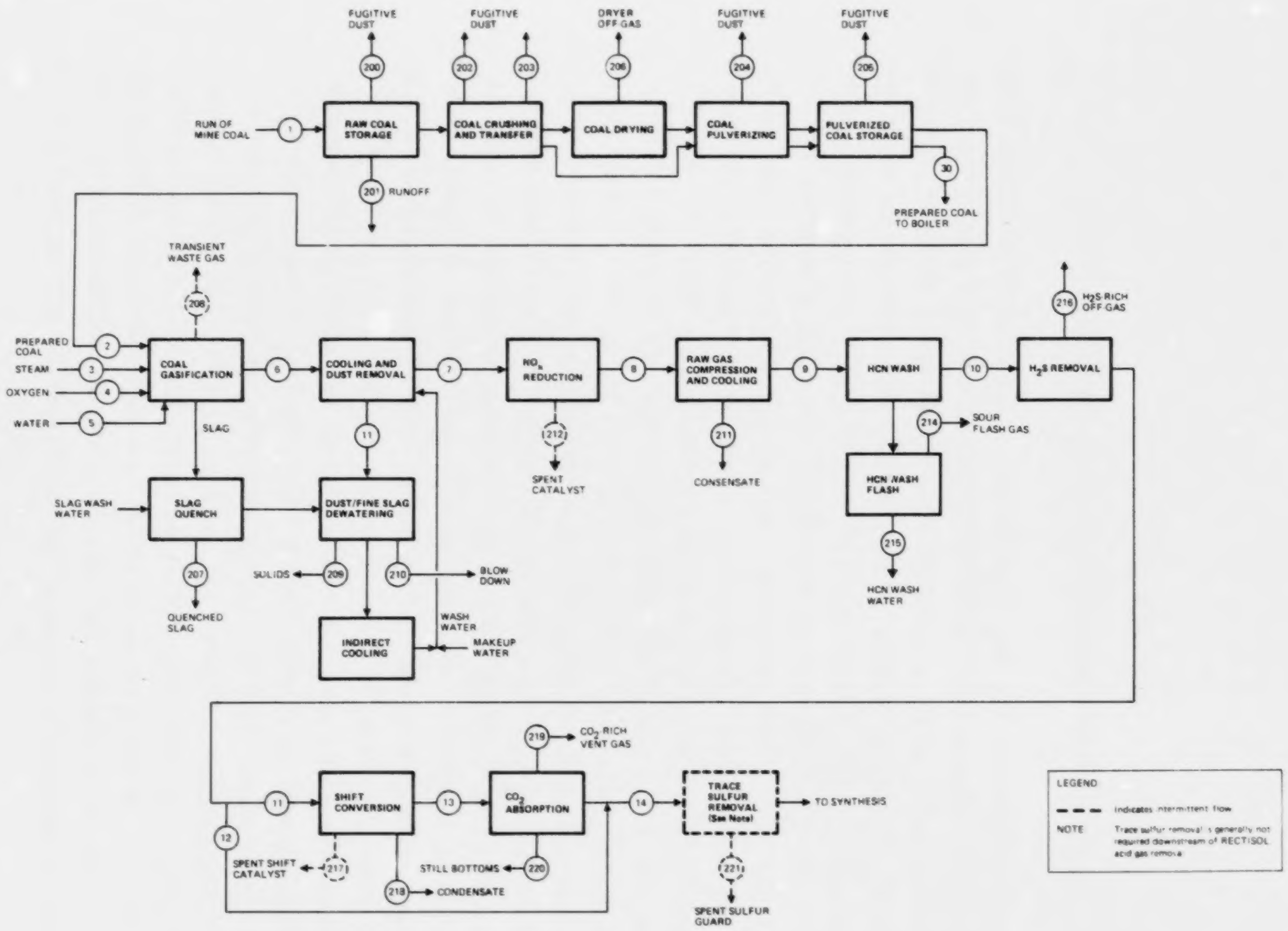

Figure 3-1. Operations associated with synthesis gas production in K-T based indirect liquefaction facilities

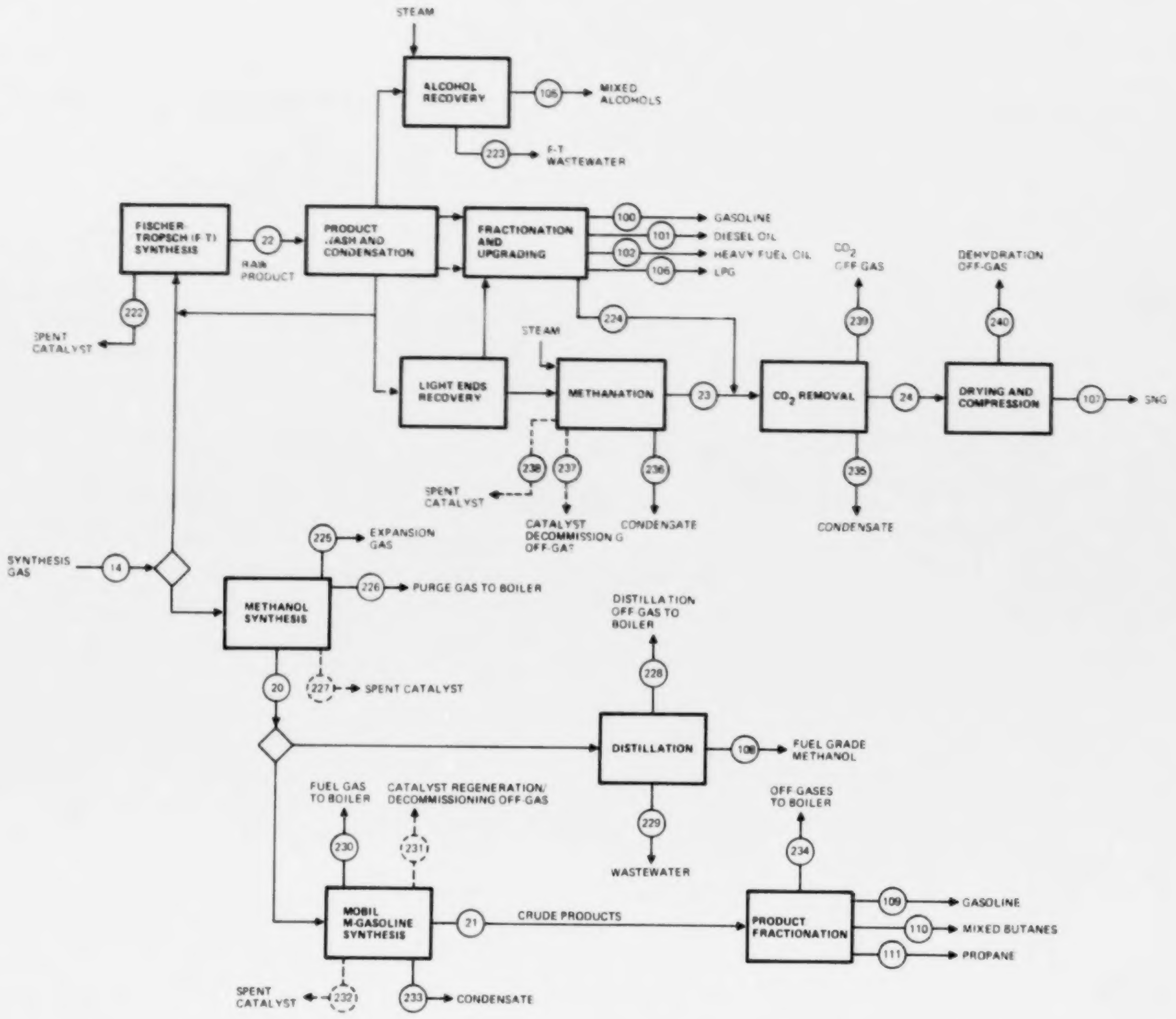

Figure 3-2. Synthesis operations associated with K-T based indirect liquefaction facilities

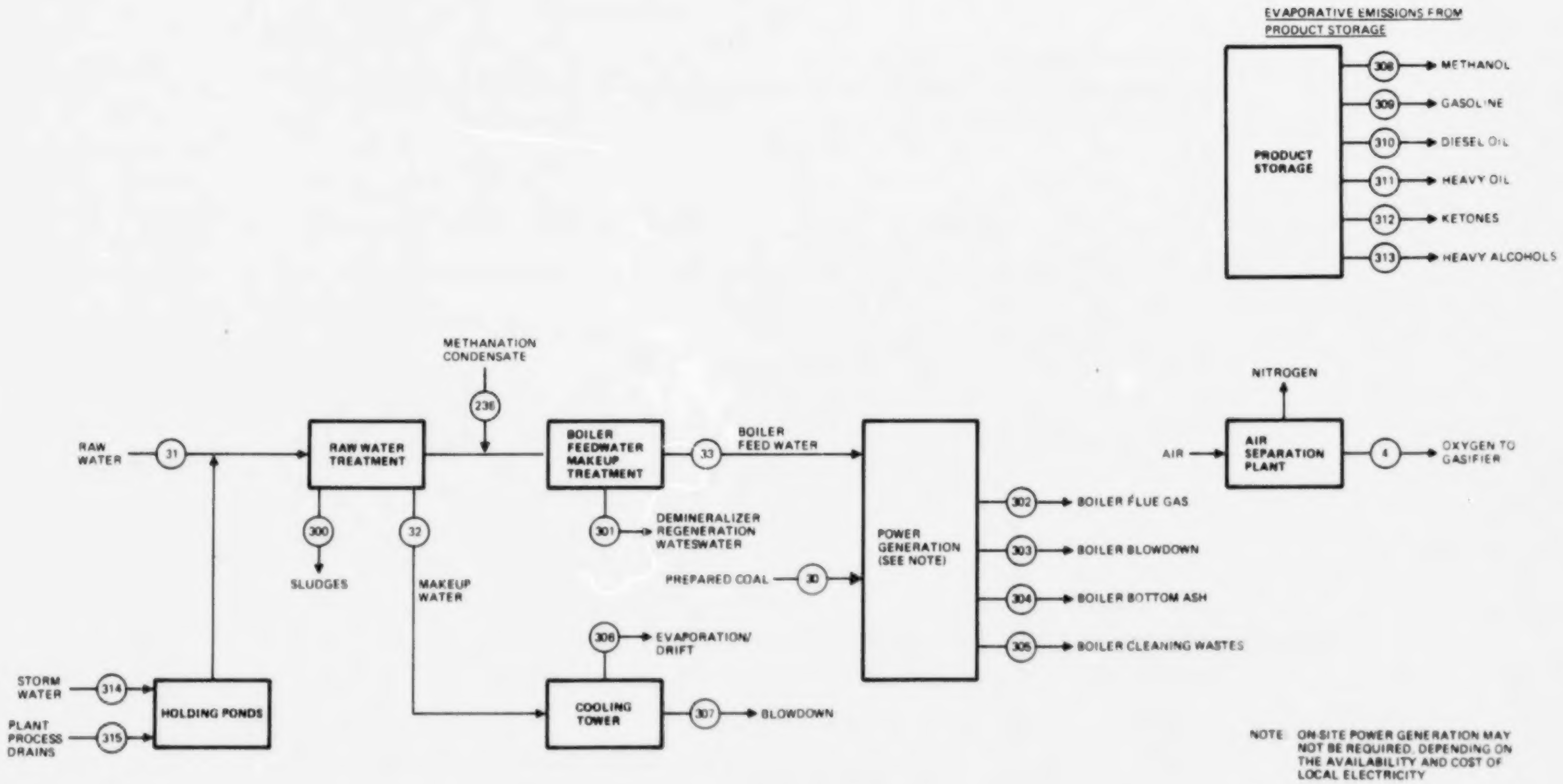

Figure 3-3. Auxiliary processes associated with K-T based indirect liquefaction facilities

to be incorporated into the first generation K-T facilities built in the U.S.

Flow estimates for major process and waste streams are presented in Table 3-1 for facilities based on an Illinois No. 6 coal. The base plant is sized for a fixed coal input to gasification. Therefore, the material flows presented for gasification and gas purification and upgrading are identical for all three synthesis alternatives considered. Since the overall thermal efficiency of indirect liquefaction differs among synthesis routes, energy to on-site auxiliary boilers for self-sufficient facilities will be strongly dependent on the specific synthesis process. To a lesser extent, this is also true with respect to material flows through coal preparation and raw water treatment. Hence, process and waste streams associated with the power boiler and most other auxiliary processes will be synthesis specific.

Numerical values presented in Section 3 are based upon both published data and engineering estimates derived from published data and material balance considerations. Material flow estimate tables in this section generally contain both published data and engineering estimates. Detailed references are provided for published data in both the text and below each table; values which are not referenced represent either summaries of published data which cannot be referenced in summary format or engineering estimates.

TABLE 3-1. FLOWS OF MAJOR STREAMS FOR K-T BASED INDIRECT LIQUEFACTION FACILITIES - ILLINOIS NO. 6 COAL*

Component Flows, kmol/hr	Prepared Coal Stream 2	Steam Stream 3	Oxygen Stream 4	Quench Water Stream 5	Quenched Slag Stream 207	Dewatered Dust Stream 209	Raw Gas From Washer Cooler Stream 7	Washer Cooler Blowdown Stream 210
H_2							5829	
CO							13699	
CO_2							1907	
N_2 + Ar							300	
CH_4							22	
S							259	
Total Dry Gas			8430				22019	
Moisture in Gas		2082					964	
Total gas, kmol/hr		2082	8430				22982	
Total Aqueous, m^3/hr	2.8			93	1.0	30		322
Total Dry Solids, Mg/hr	278				9.3	30		

(Continued)

TABLE 3-1. (Continued)

Component Flows, kmol/hr	Synthesis Feed Stream 14	Fuel Grade Methanol Stream 108	Methanol Distillation Wastewater Stream 229	F-T SNG Liquids and LPG Streams 100-107	F-T Wastewater Stream 223	Mobil-M Liquids + LPG Streams 109-111	Mobil-M Wastewater Stream 233
H_2	13664						
CO	5719						
CO_2	610						
N_2 + Ar	307						
CH_4	21						
S							
Total Dry Gas	20320						
Moisture in Gas							
Total Gas, kmol/hr	20320						
Total Aqueous, m^3/hr		0.2	9.7		159		110
Total Organic Liquids, Mg/hr		196	0.17	96	1.5	83	0.92

(Continued)

TABLE 3-1. (Continued)

Component Flows, kmol/hr	Compression Condensate Stream 211	HCN Wash Water Stream 215	HCN Flash Gas (Water Wash) Stream 214a	HCN Flash Gas (Methanol Wash) Stream 214b	H_2S-Rich Offgas Stream 216	Shift Blowdown Stream 218	CO_2-Rich Offgas Stream 219	Rectisol Still Bottoms Stream 220
H_2				0.5			46	
CO				4.4			101	
CO_2			20	1.2	269		8875	
N_2 + Ar					6		1041	
CH_4							1.2	
S			2.3	7.9	255		0.1	
Total Dry Gas			22	16	535		10064	
Moisture in Gas								
Total gas, kmol/hr			22	16	535		10064	
Total Aqueous, m^3/hr	17	238				3		1
Total Dry Solids, Mg/hr								

(Continued)

TABLE 3-1. (Continued)

Component Flows, kmol/hr	Coal to Boiler† Stream 30	Air to Boiler†	Boiler Flue Gas† Stream 302	Boiler Bottom Ash† Stream 304	Boiler Fly Ash† Stream 423
N_2 + Ar		24356	24388		
CO_2		10	4597		
O_2		6455	1065		
NO_x			12		
SO_2			69		
Total Dry Gas		30821	30133		
Moisture in Gas		651	2581		
Total Gas, kmol/hr		31472	32713		
Total Aqueous, m^3/hr	3.2				
Total Dry Solids, Mg/hr	78.7			1.8	7.6

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[*] For overview purposes, only major streams and their principal components have been included. Detailed stream characterization data are presented subsequently in this section.

[†] These streams are representative of the estimated maximum boiler size for a K-T based indirect liquefaction plant with a coal feed of 278 Mg/hr (dry basis) to the gasifier.

Section 3
Coal Preparation

3.1 COAL PREPARATION

Run-of-mine (ROM) coal is received from the mine via conveyor and stored in an active storage pile which holds a five-day supply. The five-day active storage pile (40,000 Mg for methanol synthesis case) normally provides the gasifier feed. Raw coal is also kept in an emergency storage pile containing a 30-day supply. The 30-day emergency pile (241,000 Mg for methanol synthesis case) is built up over a period of time, when coal is not required at the active storage pile, and is used if the coal supply from the mine is interrupted for an extended period of time. Coal storage piles for the Fischer-Tropsch synthesis case are approximately 16% larger than the coal piles for the methanol synthesis case. However, coal piles for the Mobil M synthesis case are approximately 4% smaller in size. These changes in size are due to the different coal feeds to the boiler in each of the three synthesis cases.

Because the K-T gasification process requires free flowing pulverized coal, some level of drying during coal preparation is necessary for all coals. The extent of drying which is required is coal specific, with residual moisture levels of approximately 1 to 2% required for bituminous coals and 8 to 10% required for lignites. Recent tests in Greece (7) indicated that drying of Illinois coal to a 1% moisture level might be required. The particle size of the feed coals to the K-T gasifier is predominantly less than 0.1mm. The allowable portion of oversize coal is about 10% in the case of bituminous coal, and 15 to 20% in the case of lignites (8). The particle size of boiler feed coal is typically 70% less than 0.075mm. Table 3-2 presents the characteristics of the Illinois No. 6 coal under consideration.

A schematic diagram of the coal preparation plant is presented in Figure 3-4. Run-of-mine coal with a top size of 10.2 cm is transported to the preparation plant by a belt conveyor. It is then transferred through the feed

TABLE 3-2. CHARACTERISTICS OF ILLINOIS NO. 6 COAL SELECTED FOR USE IN INDIRECT LIQUEFACTION BASE PLANT (9,10)

	As Revised Basis (wt %)	Dry Basis (wt %)
Moisture	10.23	
Volatile Matter	34.70	
Fixed Carbon	46.0	
Ash	9.15	10.19
C	64.16	71.47
H	4.34	4.83
O	8.1	9.02
S	2.81	3.13
N	1.21	1.35
Heating Value		
MJ/kg	26.63	29.67

Major and Minor Elements in Coal
(%, on moisture-free whole coal basis)

Al	1.20	Mg	0.04
Ca	0.92	Ma	0.060
Cl	0.28	Si	2.45
Fe	1.50	Ti	0.06
K	0.16		

Trace Elements
(ppm, on moisture-free whole coal basis)

As	1.0	Hg	1.1
B	132	Mo	7
Be	1.6	Mn	20
Br	17	Ni	14
Cd	<0.4	P	29
Co	4	Pb	10
Ce	20	Sb	0.1
Cu	12	Se	1.3
F	79	V	20
Ga	4.5	Zn	43
Ge	6.0		

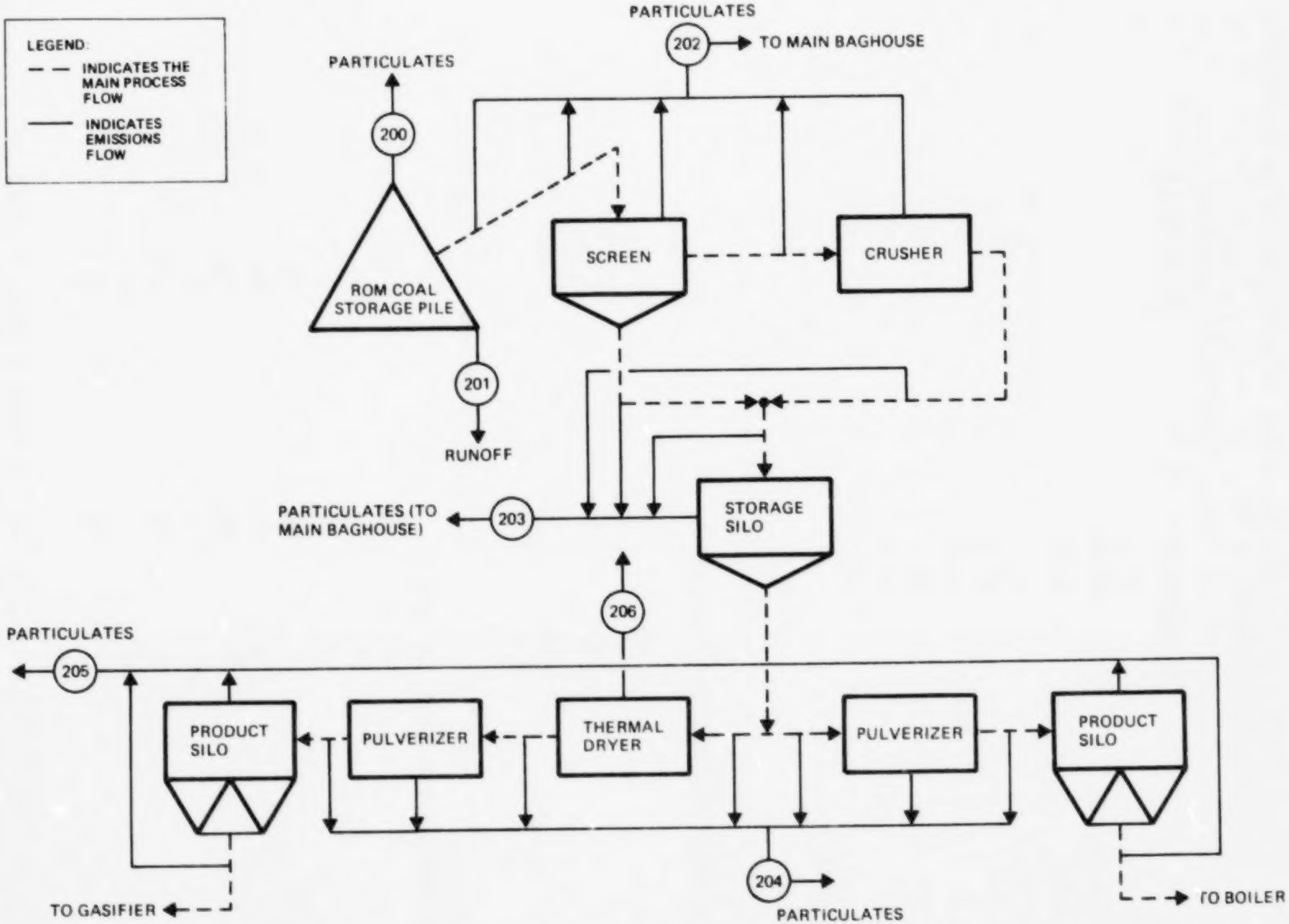

Figure 3-4. Waste streams associated with coal preparation for a K-T based indirect liquefaction facility - Illinois No. 6 coal

hopper to the raw coal screens that make a size separation at 1.9 cm. The oversize coal (10.2 cm x 1.9 cm) is conveyed to double roll crushers where it is reduced to a top size of 1.9 cm. The undersize coal from the sizing screens and the crusher product are transferred to storage silos by a belt conveyor. Coal from the storage silo is transported to the pulverizer after it is ground to 70% minus 20 mesh. The moisture content of the coal is reduced in the thermal dryer and the pulverizer from 10% to 1-2% for the K-T gasifier. Coal to the boiler does not require thermal drying since the pulverizers reduce the moisture content from 10% to a desirable 4%. The dry ground coal from the pulverizers is transferred to the product silos by gravity and then continuously fed to the boiler and K-T gasifier. Coal preparation mass flow estimates for the methanol synthesis case are presented in Table 3-3.

Major waste streams associated with the ROM coal storage and handling operations are particulate emissions from storage (Stream 200), storage pile runoff (Stream 201), particulate emissions from crushing/screening/transfer/pulverizing (Streams 202, 203, 204), and particulate emissions from prepared coal storage and feed (Stream 205). Sources of these wastes streams are shown in Figure 3-4.

The quantities of fugitive particulates generated by the five-day active and 30-day emergency storage piles are shown in Table 3-4. Emissions from coal storage piles have been investigated and results presented in several EPA reports (11,12,13). Estimates for uncontrolled emissions from various activities were compiled from information given in the references indicated in Table 3-4. Environmental assessment studies data showed relative high total suspended particulate values within 200 meters of the coal and refuse piles when compared to 24-hour primary and secondary ambient air quality standards (14,15). Ambient concentrations decrease sharply at 500 to 600 meters downwind. Particulate morphology tests showed that downwind particles were primarily a quartz material rather than coal particles indicating that the source of particulates is activity around the piles, not the coal itself. The preparation plants were found to contribute no gaseous organic matter to the environment, other than trace amounts attributable to diesel truck activity around the coal pile.

TABLE 3-3. COAL PREPARATION SECTION MASS FLOWS - METHANOL SYNTHESIS CASE

		Illinois No. 6 Coal		
	Hours per Day	Dry Basis		Moist Basis
Stream	of Operation	Mg/day	Mg/hr	Mg/hr
ROM Coal to Screen*	13	7225	556	619
Coal to Crusher*	13	4624	356	396
Coal from Screen*	13	2601	200	223
Coal from Crusher*	13	4621	356	396
Coal to Storage Silo*	13	7225	556	619
Coal from Storage Silo*	24	7225	301	335
Coal to Product Silos*	24	7225	301	305
Coal to Gasifier*	24	6682	278	281
Coal to Boiler†	24	544	23	24

*These streams increase by approximately 16% for the Fischer-Tropsch (F-T) synthesis case and decrease by 3-6% for the Mobil M synthesis case.

†Coal to boiler increases by 215% for the F-T synthesis case and decreases by 48% for the Mobil M synthesis case.

TABLE 3-4. ESTIMATED FUGITIVE DUST EMISSIONS FROM COAL STORAGE PILES

		Emission Estimates[#] (Mg/yr)	
Activity	Reference	Active Storage Piles (5-day storage)	Emergency Storage Piles (30-day storage)
Wind erosion*	12	10	57
Loading on†	13	28	28
Loading off‡	13	36	36
Vehicular activity§	13	1	6
TOTAL		75	128

*Based on a respirable emission factor of 6.4 mg of dust per kg/yr of coal stored

†Assumed activity factor of 0.75, silt content of 0.5% and Thornthwaite's precipitation index (PE) of 93 for S.W. Illinois

‡Assumed activity factor of 0.77, silt content of 0.5% and PE of 93

§Assumed activity factor of 0.5, silt content of 0.5% and PE of 93

[#] Emissions will increase by 16% for the Fischer-Tropsch synthesis case and decrease by 3.4% for the Mobil M synthesis case

Runoff streams originating from coal storage piles have been characterized in detail during environmental assessment testing programs at two coal preparation plants (14,15). The assessment results indicated that runoff water quality parameters complied with the most stringent state effluent regulations for eastern and midwestern states.

Laboratory leaching tests with raw coal and coal refuse materials have indicated that the types and quantities of pollutants released from coal storage piles are similar to those produced by coal refuse piles (16). Assuming that this similarity carries over to the pollutant loadings generated by actual refuse and coal piles, the information available from refuse pile pollutant analysis provides a source of data. In addition, there are some data available on actual effluents produced by high-sulfur coal storage piles (17). Information for these two sources, coupled with what is known about the composition of the subject coal, allows at least a range estimation of the composition of the storage pile runoff produced.

Runoff from storage piles of Midwestern coals (such as the Illinois No. 6) and Eastern coals can be highly acidic, with pH values in the range of 2 to 4, if the runoff is allowed to remain in contact with the coal for long periods of time. Total suspended solids during storm runoff can be as high as 2300 mg/L. Sulfate concentrations may be in excess of 9000 mg/L. Iron concentrations can range from 23 to 1800 mg/L, while manganese concentrations can range from 1.8 to 45 mg/L. Other elements that are at concentrations of potential concern include aluminum, mercury, arsenic, and zinc (17).

At facilities utilizing either sub-butiminous coal or lignite, runoff from the coal storage piles would be expected to be close to neutral, with a pH slightly above 7. Sulfate concentraions would probably be less than 1000 mg/L. Iron and manganese concentrations would be expected to be low, less than 0.8 mg/L for iron and below 0.4 mg/L for manganese (18). The dominant water contaminants are expected to be calcium and magnesium, with concentrations in the ranges of 200 to 400 mg/L for calcium and 50 to 250 mg/L for magnesium (19). Total suspended solids levels would probably be higher than those present in Illinois No. 6 runoff because of the tendency of these coals to slake.

Published data on particulate emissions for coal operations are limited and were taken from surface coal mining and ore mining operations, the crushed stone industry, and the manufacturing of coke. Reported emission factors (13,20) for specific operations within preparation plants are based on estimates rather than actual data. There is no consensus on the best available values for use with specific coal preparation operations. In one surface mine study, an average uncontrolled particulate emission factor of 0.2 kg/Mg of coal processed was used for loading and unloading activities in all modes of transport (21). In another surface mine investigation, a factor of 0.05 kg/Mg of coal mined was used for coal loading and unloading operations, respectively (20). The moisture contents and coal types used in these studies were not specified, and thus no distinction can be made between bituminous, sub-bituminous, and lignite coals. However, it is commonly reported that western coals and lignites generate several times as much dust as comparable amounts of eastern coal (22).

Table 3-5 provides estimates of emissions generated during the specific operations, such as unloading, crushing, and screening. The streams associated with the estimated emission values are shown in Figure 3-4.

In the absence of more specific data, simplifying assumptions were necessary in preparing these estimates. First, the same average factors were used for similar operations, such as screening, disregarding the effect of particle sizes (i.e., the same factor is used for secondary and for tertiary screening). Since the reported emission factor was based upon combined crushing/screening operations, only 50% of the published factor was used for emissions from screening alone or crushing alone. In addition, the moisture content of the coals from which the emission factors were generated was unknown; therefore, corrections for moisture content were not applied.

The quantities of particulate emissions generated by the various operations associated with the storage and subsequent handling of the screened, crushed coal are included in Table 3-5. As with crushing/screening emission factors, no distinctions have been made for differences in particulate emissions associated with lignite, sub-bituminous, and bituminous coals.

The emission factors used to calculate emissions at transfer points to the gasifier and boiler feed equipment are the same as those used for transfer points inside the preparation plant.

TABLE 3-5. PARTICULATE EMISSIONS FROM COAL PREPARATION (ILLINOIS NO. 6 COAL)

Discharge Stream Number	Emissions Source	Hours per Day of Operation	Estimated Average Emission Factors		Feed Rate As Received Basis Mg/hr	Uncontrolled Emission Rates kg/hr
			Uncontrolled kg/Mg	Reference		
202	Loading	13	Negligible	20	619	-
202	Transfer to screening	13	0.02 - 0.48	13	619	12.4 - 297‡
202	Screening	13	0.04*	13	619	25‡
202	Transfer to crushing	13	0.02 - 0.48	13	396	7.9 - 190‡
202	Crushing	13	0.04*	13	396	16‡
203	Transfer to silo	13	0.02 - 0.48	13	396	7.9 - 190‡
203	Transfer to silo from screening	13	0.02 - 0.48	13	223	4.5 - 107‡
203	Transfer to storage	13	0.02 - 0.48	13	619	12.4 - 297‡
203	Inert gas purge	13	0.02 - 0.48†	13	619	12.4 - 297‡
204	Transfer to pulverizer and thermal dryer	24	0.02 - 0.48	13	335	6.7 - 161‡
204	Transfer to Pulverizer from thermal dryer	24	0.02 - 0.48	13	290	5.8 - 139‡
204	Pulverizer	24	Negligible	13	-	-
205	Transfer to product silo	24	0.02 - 0.48	13	314	6.3 - 151‡
205	Transfer to boiler	24	0.02 - 0.48	13	24	0.5 - 11.5§
205	Transfer to gasifier	24	Negligible	13	290	-
205	Inert gas product silo purge	24	0.02 - 0.48†	13	314	6.3 - 151‡
206	Thermal dryer	24	10	13	290	435

*Emission factor as reported for combined "secondary crushing/screening operations" is 0.08 kg/Mg of coal processed. Assumed contribution from crushing is equal to that from screening and is thus equal to 0.04 kg/Mg of coal processed.

†Assume same emission factor as that of transfer.

‡Emissions from these streams increase by approximately 16% for the Fischer-Tropsch synthesis and decreases by 3-4% for the Mobil-M synthesis case.

§Emissions from this stream increase by 215% for the Fischer-Tropsch synthesis case and decrease by 48% for the Mobil-M synthesis case

Emissions from Thermal Dryers (Stream 206)

In a thermal dryer, hot gas from a furnace is forced past wet coal in the drying chamber to volatilize coal moisture. Drying gas is generated by combustion of coal or fuel gas. In the case of coal combustion, dryer off-gases would be similar in composition to flue gases from the boiler system with respect to gaseous pollutants such as SO_x, NO_x, and CO. Particulate loadings would be higher due to entrainment of dried coal. Low Btu fuel gases available for coal drying purposes at this type of facility are expected to be essentially free of sulfur and nitrogen compounds. The gaseous pollutants associated with use of these gases from thermal drying are NO_x and CO. The exact quantity of dryer offgases generated is dependent upon the quality of dryer fuel used, ROM coal moisture, and residual coal moisture requirements. The composition of dryer offgases with respect to SO_x, NO_x, and CO is dependent upon the quality of dryer fuel used, and is not unique to the coal preparation operation; offgas compositions will be discussed in conjunction with auxiliary combustion processes (Section 3.6.2). It should be noted that offgases from coal drying may contain low levels of volatile organic compounds (VOC), although essentially no data are available regarding such emissions.

The amount of coal particles entrained in the drying chamber exit gas stream is significant. One study estimated an uncontrolled particulate emission factor from thermal dryers to be 10 kg/Mg of coal dried (23). In order to recover these substantial quantities of dry airborne product coal, mechanical collectors are generally included as process equipment for thermal dryers. Uncontrolled fugitive emissions from the dryer were calculated and are assumed to be those from the mechanical collector outlet. For a gasifier feed rate of 290 Mg/hr uncontrolled emissions from the thermal dryer are estimated to be 435 kg/hr.

3.2 COAL GASIFICATION

Gasification consists of the partial oxidation of pulverized coal to produce raw synthesis gas. The Koppers-Totzek (K-T) process is characterized by low pressure (slightly above atmospheric), entrained-flow slagging coal gasification, featuring rapid partial oxidation of pulverized coal in a stream of oxygen and steam. Flame temperatures may range from 2000-2300K during gasification, with reactor temperatures of 1500-1900K (7,24,25,26). The gasifier is a double-walled, water-cooled steel vessel with a refractory lining. Low pressure steam is generated in the water cooling system for process use. While older commercial installations utilize a two-headed gasifier configuration resembling an ellipsoid with horizontally opposing burners at the apices, the newest installations (three gasifiers each at Ramagundam and Talcher, India) employ four-headed gasifiers. The four-headed configuration resembles two intersecting ellipsoids with burners located 90 degrees apart at each of the four apices. Essentially all ranks of dried coal (1 to 8% moisture) with ash contents of up to 40% can be gasified. Four-headed K-T gasifiers are capable of processing up to 800 Mg of coal per day.

The K-T gasification process is depicted in Figure 3-5. A mixture of dried, pulverized coal, low pressure steam, and high purity oxygen are continuously injected into the gasifier with injection speeds exceeding flame propagation speeds to prevent flash back. Coal is introduced into the gasifier through screw feeders at the burner heads. This system provides for (1) a high degree of turbulence and mixing; (2) continuous ignition should one burner become temporarily blocked; (3) flue gases being directed into the center of the gasifier, thus minimizing hot spots in the refractory lining; and (4) unreacted coal particles from one flame region being gasified in the opposing region. Reaction between the coal and oxygen upstream of the gasification zone is inhibited by maintaining moderate temperatures in the mixing nozzles through circulation of cooling water. The gasification

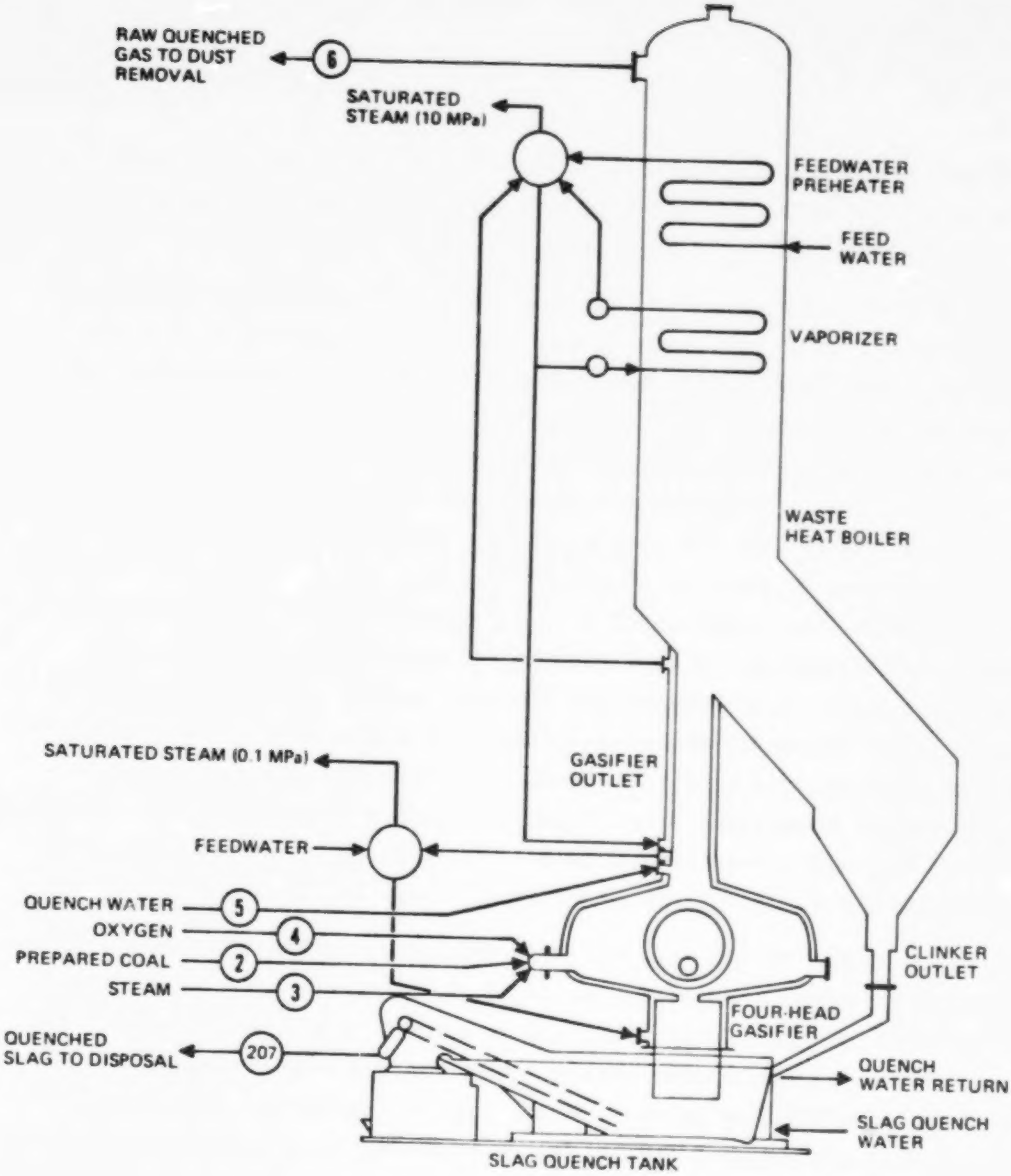

Figure 3-5. GKT's gasifier with waste heat boiler and slag extraction system (26,27)

reactions occur in a cocurrent stream of suspended coal particles, with raw product gas and entrained particles exiting the gasifier vertically. Coal residence time in the gasifier is less than one second.

Coals vary widely in terms of their reactivity or degree of carbon conversion to useful gas (CO plus H_2) as a function of temperature in a K-T gasifier. Coals also differ greatly in their ash fusion temperatures and molten ash viscosities. The temperature of gasification for a particular coal in a K-T gasifier is largely dictated by the coal ash properties since a layer of slowly flowing molten slag must be maintained on the sides of the gasifier to protect the refractory lining. Temperature control in the gasifier is achieved by addition of moderating steam along with oxygen. Lignitic coals commonly show higher reactivities (low gasification temperatures for high carbon conversion) at the temperatures needed for proper slag flow. Bituminous coals require higher gasification temperatures than lignites to obtain a high degree of carbon conversion, and thus the ash (slag) behavior in such coals is more critical. Generally, lower rank coals will show higher carbon conversions in a K-T gasifier than higher rank coals. Unreacted carbon along with a fraction of the original coal ash exits the gasifier as dust entrained in the hot raw product gas (Stream 7).

That portion of the coal ash which impinges as molten slag on the gasifier walls eventually exits the bottom of the gasifier into a quench tank. Circulating cold water causes the slag to shatter into a granular form, and a continuous conveyor system removes the granulated slag (Stream 207) from the tank. The relative amounts of coal ash exiting the K-T gasifier as slag or dust varies among coals. The dust-to-slag ratio (carbon free basis) can be as low as 1:10 for some lignites, and as high as 2:1 for some bituminous coals.

The composition of K-T gas has been measured at commercial facilities gasifying Indian bituminous coal (28), South African sub-bituminous coal

(8,24,29), and Turkish lignite (8,30). Gas characterization data are also available from commercial-scale gasification tests performed with an Illinois No. 6 coal (7) and with Char-Oil-Energy Development (COED) process chars derived from Western Kentucky and Pittsburgh seam coals (25). These data indicate that the bulk composition of K-T gas is determined by the water-gas equilibrium and the relative amounts of coal, steam, and oxygen. Raw gas consists of 55-65% CO, 25-30% H_2, and 6-12% CO_2 on a dry basis. Small amounts of CH_4 are present in K-T gas (ppmv levels) but no tars, oils, phenols, or high molecular weight organics have been found. Coal sulfur is largely gasified forming H_2S and COS at a ratio of about 9:1. Traces of CS_2 and SO_2 are also found. A fraction of the original coal sulfur will also be contained in the slag and dust in the raw gas. Nitrogen in the coal is mostly converted to elemental nitrogen (over 90%), although side reactions also lead to the formation of NH_3, HCN, and NO in the ppmv range. Limited data indicate that ammonia levels are higher with low rank coals than with high rank coals, but the data do not show a convincing similar trend in the case of HCN.

Water sprays are utilized at the gasifier outlet to reduce the gas temperature to below the ash fusion temperature, approximately 1360-1500K. This solidifies molten entrained dust to prevent its adherence to waste heat boiler tubes. Raw product gas exiting the gasifier flows vertically through a waste heat boiler system producing high pressure steam, thereby recovering heat rejected by the gasifier, and cooling raw gas to approximately 570K. Material flow estimates for the coal gasification operation are presented in Table 3-6.

Quenched Slag (Stream 207) and Slag Quench Water

K-T slag is a coarse, pebble sized material which is physically stable and essentially chemically inert. Due to the irregular surfaces/shapes which form during slag solidification in the quench tank, the material can be crushed and broken somewhat by handling and compacting. Quenched slag retains about 10% moisture.

TABLE 3-6. MATERIAL FLOW ESTIMATES FOR K-T GASIFICATION (ILLINOIS NO. 6 COAL)*

	Prepared Coal Stream 2		Steam Stream 3		Oxygen Stream 4		Quench Water Stream 5		Quenched Slag Stream 207	Raw Quenched Gas Stream 6	
	kmol/hr	kg/hr	kmol/hr	kg/hr	kmol/hr	kg/hr	kmol/hr	kg/hr	kg/hr	kmol/hr	Vol
H_2										5829	26.4
CO										13699	62.1
CO_2									0.4	1910	8.7
CH_4										22	998 ppmv
H_2S									0.001	229	1.0
COS										26	1166 ppmv
CS_2										2	89 ppmv
SO_2										0.5	21 ppmv
$SO_4^=/S_2O_3^=$									0.4		
SO_3									0.03		
O_2					8261	264342					
HCN									0.01	2.6	118 ppmv
HSCN									0.004		
NO										0.07	3 ppmv
NH_3									0.16	4.0	180 ppmv
N_2					65	1817				196	0.9
Ar					104	4145				104	0.5
Cl	22	780							2.2	22	998 ppmv
F	1.3	22							0.07	1.3	58 ppmv
Total Dry Gas										22047	
H_2O	156.1	2810	2082	37500			5134	92496	1037	7919	
Ash		28400							9245	18351 kg/hr	
Coal (MAF)		250000									
C	16565	198970							48	10805 kg/hr	Dust
H	13343	13450								30 kg/hr	
S	272	8710							38	419 kg/hr	
O	1519	24308									
N	268	3760									
Total: kmol/hr			2082		8430		5134			29966	
kg/hr		281210		37500		270303		92496	10371	672242	
Temperature(K)									300	450	
Pressure(MPa)									0.1	0.1	

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* The number of significant figures shown in some cases do not represent the degree of accuracy and are retained for material balance purposes only. Nevertheless, slight imbalances do appear as a result of numerical rounding. Material flow estimates and stream compositions are based upon published data and engineering estimates. Tabulated data are based upon references 7, 8, 24, 25, and 29.

Slag from the gasification of Illinois No. 6 coal has essentially the same overall composition as that of the parent coal ash. The quenched slag contains about 0.5% carbon by weight (7). Quenching of the slag is integral with gasification and involves intimate contact with circulating water (e.g., from gas cooling and dust removal); hence slag from the quench tank is leached of any readily soluble material. Table 3-7 summarizes the results of leaching tests on quenched slag from K-T gasification of an Illinois coal at the Nitrogenous Fertilizer Industry (NFI), Ptolemais, Greece (31). The NH_3, SCN^-, and COD values shown in Table 3-7 reflect residuals derived from washer cooler water used for slag quenching. Such species are not believed to be present in measurable amounts when non-process water is used for quenching or for rinsing the quenched slag.

TABLE 3-7. RESULTS OF K-T SLAG LEACHING TESTS (31)

	Concentration in mg/kg Slag	
Element	RCRA Extract pH 5	ASTM Neutral Extract pH 7
Ag	<0.2	<0.2
As	<8	<8
Ba	<0.2	<0.2
Cd	<0.1	<0.1
Cr	<0.8	<0.8
Hg	<0.004	<0.004
Pb	<1	<1
Se	<8	<8
NH_3		14
SCN^-		<2
COD		100

The slag generation rate in the example case is about 9300 kg/hr. About 30 kg of cooling (or quench) water are needed for each kg of slag. Since the slag is essentially non-leachable, the quality of water leaving the quench tank is determined primarily by the quality of input water. In existing K-T plants the input water is the same as input to gas cooling (see Section 3.3.1) since slag and wash waters are treated together in common solids settlers and direct contact cooling towers. The slag quench flow in such systems amounts to only a few percent of the total water flow. As mentioned previously, "clean" water may be used for slag quenching and/or slag may be rinsed to minimize the slag loading of undesired species (e.g., CN^- or NH_4^+). Thus, the slag quench water is not viewed as a separate waste stream but rather as an integral part of the overall wash circuit. In fact, the slag quench tank may be a point of makeup to the water circuit. The very small amounts of pollutant species actually contributed to the water during slag quenching exit the system with cooling and dust removal blowdown.

Transient Waste Gases (Stream 208)

For short periods of time during startup, shutdown, and transient operation, gases are generated which are not of use in downstream processing. Startup of a K-T gasifier generally features use of fuel oil and oxygen under essentially stoichiometric conditions to accomplish gasifier heatup. The combustion gases are vented to the atmosphere through startup stacks. Generally, less than one-half hour is needed to start a gasifier from a cold state, and emissions during most of this period are representative of combustion rather than gasification conditions. Startup of a gasifier which is still warm from earlier operation can be accomplished in as little as five minutes. During upsets or shutdowns, the gasifier system is flooded with inert nitrogen to purge combustibles. Thus, the entire gas volume of the gasifier/waste heat boiler system is vented to the atmosphere in just a few seconds. These gases will contain all of the components of raw K-T gas (Table 3-6) along with the purge nitrogen.

At present, no data are publicly available relating to characteristics of transient gases or to the quantities which might be encountered in K-T facilities. All existing facilities are provided with vent stacks for such gases, although no further control (e.g., flaring) is effected other than discharge away from the immediate areas where personnel may be exposed. The transient waste gases are generally viewed as more of an occupational safety problem than as a pollution problem since the actual mass emissions represented are very small on an average basis. Since a relatively large volume of such gases can be released in a very short period in a small area, K-T plant designs reflect concern for safety of operating personnel.

3.3 GAS PURIFICATION AND UPGRADING

The gas purification and upgrading operation consists of: (1) gas cooling and dust removal to remove some of the volatile contaminants (e.g., ammonia, chloride, fluoride, and some fraction of the cyanide) and all dust from the raw K-T gas; (2) NO_x reduction for control of traces of NO_x present in the raw gas; (3) raw gas compression and cooling to compress the raw K-T gas to a pressure suitable for downstream operations; (4) shift conversion to obtain the hydrogen to carbon oxides ratio required for liquid product synthesis; (5) acid gas removal for removal of sulfur compounds and carbon dioxide; and (6) removal of trace sulfur compounds which may be present in the synthesis gas.

Contaminants removed from the raw K-T gas during purification and upgrading operations become components of various waste streams. Thus, purification and upgrading operations generate several of the most important waste streams in an integrated facility from the standpoint of waste characteristics and volumes. The ensuing sections provide details on the nature of specific processes and their associated waste streams.

3.3.1 Gas Cooling and Dust Removal

Raw K-T gas from the waste heat boiler contains entrained dust which must be removed prior to compression and downstream processing. Because primary dust removal is effected by water washing, gas cooling is an integral part of the dust removal operation. The gas cooling and dust removal operations are presented schematically in Figure 3-6. Hot raw gas from the waste heat boiler is cooled and scrubbed of entrained dust in two stages. The first stage consists of a washer cooler which reduces the gas temperature and provides bulk dust removal by means of direct water scrubbing. Additional cooling and dust removal are subsequently achieved in Thiesen disintegrators and droplet separators. The gas temperature is reduced from about 570K to 300K during these washing operations. Blowers downstream of the

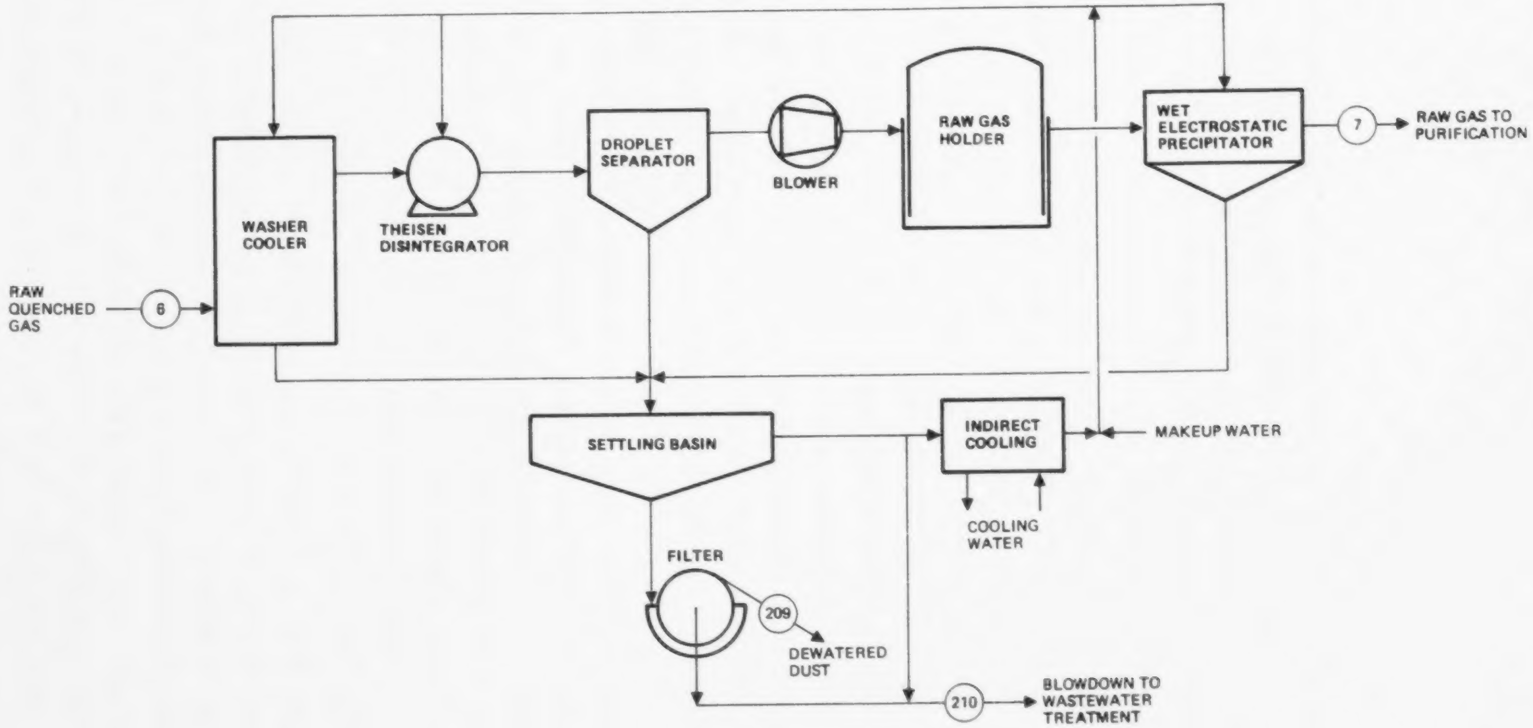

Figure 3-6. Gas cooling and dust removal

droplet separator compress the gas for transport to the raw gas holders. The gas holders provide for a continuous, uniform gas feed rate to the downstream operations (e.g., compression). Final dedusting is provided by a wet electrostatic precipitator (ESP) which can reduce the raw gas dust content to less than 0.2 mg/m^3 of raw gas (7).

Dust collected in the washer cooler, droplet separator, and wet ESP is pumped to settling basins for thickening. Most of the clear water overflowing the settlers is indirectly cooled and recycled (although all existing K-T gasification facilities utilize cooling towers for wash water cooling, commercial designs for U.S. facilities feature indirect cooling to eliminate the potential for volatilization of pollutants such as NH_3 and HCN). The settler underflow is filtered to produce dewatered dust (Stream 209) and filtrate which is combined with a portion of the clarifier overflow as blowdown (Stream 210) for controlling of dissolved component buildup. Makeup water required to maintain the system water balance is added to the recycle wash water stream to minimize corrosion in the washer cooler, disintegrator, droplet separator, and wet ESP. Material flow estimates for key streams in the gas cooling and dust removal process are presented in Table 3-8. It should be noted that dewatering of carbonaceous dusts using fuel oil to displace dust moisture has been demonstrated in conjunction with coal gasification and petroleum refining industries. This approach is not considered in this manual because developers indicate that it is economically unattractive in these applications due to the associated fuel oil consumption.

Waste streams from gas cooling and dust removal are the dewatered dust (Stream 209), and cooling and dust removal blowdown (Stream 210). The dust from gasification is typically disposed of in settling ponds. However, large land requirements can be associated with such ponding. Further, in the case of higher rank coals, gasification dust may contain 6% or more of the feed coal carbon. Therefore, a filtration step has been included in the design gas cooling and dust removal process to reduce both area requirements and/

TABLE 3-8. MATERIAL FLOW ESTIMATES FOR RAW GAS COOLING AND DUST REMOVAL PROCESSES (ILLINOIS NO. 6 COAL)*

	Raw Quenched Gas Stream 6		Raw Gas From Washer Cooler Stream 7		Dewatered Dust Stream 209		Blowdown to Wastewater Treatment Stream 210	
	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	kg/hr	kmol/hr	mg/L
H_2	5829	26.4	5829	26.5				
CO	13699	62.1	13699	62.2				
CO_2	1910	8.7	1907	8.7	0.3	12	2.9	403
CH_4	22	998 ppmv	22	999 ppmv				
H_2S	229	1	229	1.0	0.001	0.03	0.009	1
COS	26	1166 ppmv	26	1168 ppmv				
CS_2	2	89 ppmv	2	89 ppmv				
SO_2	0.5	21 ppmv	0.1	6 ppmv				
$S_2O_3^=$					0.03	3.0	0.3	103
$SO_3^=$					0.009	0.74	0.1	25
$SO_4^=$					0.08	7.5	0.85	254
HCN	2.6	118 ppmv	2.5	113 ppmv	0.008	0.2	0.08	7
HSCN					0.002	0.1	0.02	4
NO	0.07	3 ppmv	0.07	3 ppmv				
NH_3	4.0	180 ppmv	0.75	34 ppmv	0.27	4.6	2.9	156
N_2	196	0.9	196	0.9				
Ar	104	0.5	104	0.5				
Cl^-	22	998 ppmv	1	50 ppmv	1.8	62.3	19	2111
F^-	1.3	58 ppmv	0.06	3 ppmv	0.1	2.0	1	66
Total Dry Gas	22047		22019					
H_2O	7919		964		1639	29520	17843	
Dust	29605 kg/hr					29605		
Total: kmol/hr	29966		22982		1641		17870	
kg/hr	672242		516351			59217	322448	
Temperature(K)	450		300		310		310	
Pressure (MPa)	0.1		0.1		0.1		0.1	

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*The number of significant figures shown in some cases do not represent the degree of accuracy and are retained for material balance purposes only. Nevertheless, slight imbalances do appear as a result of numerical rounding. Material flow estimates and stream compositions are based upon published data and engineering estimates. Tabulated data are based upon Reference 7.

or improve the feasibility of dust combustion prior to disposal. For flow estimating purposes, gasification dust from Illinois No. 6 coal has been assumed to settle to about a 20% solids slurry and be further concentrated to 50% solids by filtration, although a higher degree of dewatering (65% solids) has been indicated in a similar design for K-T gasification of a subbituminous coal (4).

Blowdown from the gas cooling and dust removal operation may be required to maintain a system water balance and/or to prevent excessive buildup of soluble components in the wash water. Thus, as a minimum, the blowdown stream would remove that portion of the unreacted gasification steam and quench water condensed during gas cooling which is not removed with the gasification dust. The blowdown of any additional water must be accompanied by the addition of a corresponding amount of makeup water and serves to lower the level of dissolved solids in the washer circuit. Because the quantities of gasification steam, quench water, and water soluble ash/dust components are coal specific and because the quantity of water removed from the washer system with the dust is both coal and process specific, the quantity of blowdown required is therefore both coal specific and process specific. The blowdown quality is determined by the coal characteristics and to a lesser extent, the makeup water characteristics.

Slag quench water may be incorporated into the gas cooling and dust removal water circuit through the settling basin used for fine slag settling and cooling purposes. Alternatively, the slag quench system could utilize a separate settling/cooling circuit which would tend to minimize the level of contaminants (particularly NH_3, HCN, Cl^-, and F^-) present in the slag moisture. In this case, slag quench water may be suitable for use as makeup water to the gas cooling and dust removal circuit. In either case, specifics of the slag quench/gas cooling and dust removal interconnection have little effect on either the flow or quality of the dewatered dust (Stream 209) and blowdown (Stream 210) streams since slag quench consumes a negligible amount of process water and is not likely to contribute significantly to levels of dissolved ammonia, cyanide, chloride, and fluoride.

Dewatered Dust (Stream 209)

Dust entrained in raw K-T gas consists of very small particles (mean diameter about 0.03 mm) containing ash and ungasified carbon from the feed coal. When the dust is removed by water washing, a water slurry is generated which is normally sent to clarification. Clarifier underflow contains around 20% solids and can be dewatered further by simple gravity thickening in holding ponds or by mechanical means. The final moisture content of dewatered dust depends largely upon the dust characteristics (particularly its carbon content) and the method of dewatering employed. Regardless of the exact moisture content, the dewatered material has a relatively low density when compared to slag or combustion ash. It also has poor mechanical stability, and upon rewetting, exhibits tendencies toward plastic flow and/or gravity settling.

Elemental analyses of the dry dust from Illinois No. 6 coal gasification indicate that the dry dust contains approximately 36% carbon, 0.1% hydrogen, and 1.4% sulfur (7). Ash present in the dust has essentially the same composition as that of the coal ash, although it is substantially depleted of volatile elements such as chlorine and fluorine. Ash in the dust corresponds to approximately 67% of the total coal ash to gasification.

Since the dust particles are very small and experience thorough contact with wash water for at least a few minutes, it is expected that most of the readily soluble material in the dust will be leached. Further, the remaining interstitial water in dewatered dust will contain constituents derived from wash water used in the quench circuit. Table 3-9 presents the available data on the leachability of selected elements in dry K-T dust, wet (dewatered) K-T dust, and, for comparison purposes, the parent coal.

The dry dust was collected using a cyclone for test purposes only. The data show that for Ag, Cr, Hg, Pb, and Se, readily soluble levels are near or below analytical detection limits in all of these solid materials. Detectable amounts of Cd, As, and Ba are leachable from the dry dust. Based upon elemental balance considerations, mass loadings of trace elements per unit weight of dry material in extracts of dry dust would be expected to be greater than or equal to those in extracts of wet dust. Boron is highly leachable from both the dry dust and the parent coal. Chromatographable organics, including priority organic pollutants have not been detected in wet K-T dust (32,34).

TABLE 3-9. LEACHABILITY OF SELECTED ELEMENTS FROM K-T DUST AND FROM ILLINOIS NO. 6 FEED COAL[‡]

Element	Dry K-T Dust (31)* RCRA (pH 5)	Dry K-T Dust (31)* ASTM (pH 7)	Wet K-T Dust (32)[†] RCRA (pH 5)	Illinois No. 6 Coal (33) RCRA (pH 5)	Illinois No. 6 Coal (33) ASTM (pH 7)
Ag	<0.2	<0.2	<0.2	<0.2	<0.2
As	<7	5.6	0.04	<8	<8
B	44	340	--	58	114
Ba	0.4	2.4	<2	1.0	16
Cd	<0.14	11	0.6	2	--
Cr	<0.4	<0.4	0.02	<0.4	--
Hg	<0.004	<0.004	<0.004	<0.004	<0.004
Pb	<3	<3	0.26	<3	--
Se	<16	<13	<0.02	<8	--

*Collected by a cyclone for test purposes only; dry dust collection is not employed in conventional plants

[†] 34% solids basis

[‡] Units are mg/kg solid

Not indicated in Table 3-9 are components which are associated with the wash water as a result of scrubbing gaseous constituents from the raw gas stream; these include Cl^-, F^-, CN^- (and, indirectly, SCN^-), NH_4^+, and $S^=$.

The exact levels of these species are dependent upon the coal type and the water management plan for the washer cooler. Wash water associated with the dewatered dust is expected to have the same composition as cooling and dust removal blowdown (Stream 210), discussed below.

Cooling and Dust Removal Blowdown (Stream 210)

If water quality were not a concern in the wash water circuit, it could, in principle, be possible to eliminate an aqueous blowdown by internal recycle. In such a case, water would only leave the system with dewatered slag and dust. However, constituents derived from coal, particularly chlorine, will concentrate in the wash water and limit the ability to internally recycle all of the wash water due to corrosion and scaling considerations. Further, in the case of high chlorine, low alkalinity ash coals, such as the example coal in this document, pH control with caustic or lime would be necessary in the wash circuit. The sodium or calcium added for pH control will contribute to the dissolved solids load of the wash water, affecting the quantity of blowdown needed. Thus, blowdown quantity is dependent upon the coal characteristics and water quality requirements for the washer cooler system.

For purposes of analysis, it has been assumed that levels of Cl^- exceeding around 2000 mg/L would be unacceptable from a corrosion standpoint. Given the Cl level in the subject coal (2800 ppm), a blowdown of 322 m^3/hr was estimated. For coals with different Cl levels, the corresponding blowdown would differ proportionally. The estimated characteristics of the blowdown in the case of the subject coal are presented in Table 3-10. Principle potential pollutants are NH_4^+, CN^-, and reduced sulfur species. The net production of these species is not thought to be greatly different among coals, so that their concentrations will be similar for most coals when blowdown rates are similar. Also, heavy elements such as As and Se will be present, but levels are highly coal specific.

TABLE 3-10. CHARACTERISTICS OF BLOWDOWN FROM COOLING AND DUST REMOVAL (7,34)

Major Constituents/Gross Parameters	mg/L	Organic Constituents/Parameters	mg/L
NH_4^+ (as NH_3)	156	Total Chromatographable Organics	<0.1
CN^-	7	Oil & Grease	1.3
SCN^-	4	Phenols	<0.001
$S_2O_3^=$	103	Formate	<0.1
$SO_3^=$	25	COD	100**
$SO_4^=$	254	TOC	<10**
$S^=$	1		
Cl^-	2111#	Trace Elements	
Na^+	1000*	F	66#
Ca^{++} plus Mg^{++}	--†	B	100‡
TDS	4200**	As	<1
pH	7§	Se	<1
		Ag	<0.02
		Ba	0.04
		Cd	<0.01
		Cr	<0.01
		Hg	<0.001
		Pb	<0.03

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* Added in the form of NaOH to water system for pH control, also influenced by makeup water quality

† Highly influenced by makeup water quality as well as ash characteristics

‡ Dependent upon clarifier design

§ Without pH control the wash water would be acidic for high chlorine, low alkalinity ash coals

# Estimated from raw coal analysis and assuming that all of the amount in the raw coal will report to the wash water

** Calculated from contributing constituents

Since essentially no non-methane organics are produced in K-T gasification, no measurable levels of chromatographable organics have been found in K-T wastewaters. All COD and TOC in these wastes can be attributed to reduced sulfur and nitrogen species. Some suspended carbonaceous dust will remain in the blowdown; the exact amount depends heavily upon the clarifier and filter designs.

3.3.2 NO_x Reduction

Operating data from Modderfontein (29) have indicated fouling of compressor components and the acid gas removal unit which is attributed to the presence of nitrogen oxides and O_2 in the raw synthesis gas. Fouling in the compressor resulted in reduced heat transfer in intercoolers, and, occasionally, vibration due to rotor imbalance. Fouling in the acid gas removal columns resulted in reduced solvent circulation rates, and fouling of the heat exchangers resulted in insufficient cooling capability to achieve the required degree of gas purification. Generation of fouling deposits was attributed to the following reactions:

$$Fe + H_2S \rightarrow FeS + H_2$$

$$4FeS + 7NO \rightarrow Fe_4S_3(NO)_7^- + S \qquad \text{(Roussin's salt)}$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO_2 + 2H_2S \rightarrow 2H_2O + 2NO + 2S$$

Although several operating modifications had been employed to permit stable process operation, final resolution was achieved by catalytic reduction of nitrogen oxides in the process gas. Reduction of nitrogen oxides is achieved by passing compressed gas through a reactor containing a cobalt molybdate catalyst. Therefore, a nitrogen oxide reduction reactor has been included in the base plant design. For balance purposes it has been assumed that NO in the raw gas is catalytically hydrogenated to produce N_2 and H_2O;

data regarding this unit's performance and reaction chemistry are not publicly available. Some degree of gas compression preceding the NO_x catalytic reactor would be required to reduce unit size and promote the desired reaction. For simplicity, raw gas compression is shown to follow NO_x reduction in Figure 3-1 since this is where most of the compression would occur.

Material flow estimates for NO_x reduction, raw gas compression, and HCN wash steps are presented in Table 3-11. In addition to essentially complete NO_x destruction, some conversion of HCN to NH_3 and CO is also known to occur over the catalyst. For analysis purposes, and due to lack of publicly available data relating to such HCN conversion , the material flow in Table 3-11 indicates no HCN destruction in the subject unit.

Spent NO_x Reduction Catalyst (Stream 212)

The only waste stream expected from this reactor is spent catalyst. Since no experience has been documented for this reaction system, the quantity of spent catalyst requiring disposal and its physical/chemical characteristics are currently unknown. However, based upon experience with shift conversion catalysts, approximately 80 Mg of spent catalyst would be generated every 3 to 5 years.

3.3.3 Raw Gas Compression and Cooling

Koppers-Totzek technology involves coal gasification at essentially atmospheric pressure. However, the NO_x reduction, cyanide wash, shift conversion, and acid gas removal (particularly in the case of physical absorption processes) processes are more efficient and economical at elevated pressures. Therefore, raw gas is compressed to about 3 MPa prior to subsequent treatment. The temperature rise of the gas during compression is controlled by intercoolers and an aftercooler, consistent with compressor materials limitations and temperature requirements of downstream processes. Raw gas compression and cooling are depicted schematically in Figure 3-7. Waste streams from raw gas compression and cooling are condensate (Stream 211) and

TABLE 3-11. MATERIAL FLOW ESTIMATES FOR K-T NO_x REDUCTION, COMPRESSION AND COOLING, AND CYANIDE WASH PROCESSES (ILLINOIS NO. 6 COAL)*

	Raw Gas From Washer Cooler Stream 7		Raw Gas After NO_x Reduction Stream 8		Compression Condensate Stream 211		Raw Compressed Gas Stream 9		Compressed Gas After HCN Wash Stream 10		HCN Wash Water Water Wash Case Stream 215†		Cyanide Wash Flash Gas Water Wash Case Stream 214a†		Cyanide Wash Flash Gas Methanol Wash Case Stream 214b‡		Aqueous Cyanide Wash Still Bottoms Methanol Wash Case Stream 213‡	
	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	mg/L	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	mg/L	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	mg/L
H_2	5829	26.5	5829	26.5			5829	26.5	5829	26.5					0.49	3.0		
CO	13699	62.2	13699	62.2			13699	62.2	13699	62.3					4.4	26.4		
CO_2	1907	8.7	1907	8.7	0.7	1900	1907	8.7	1873	8.5	11.4	2111	19.7	89.3	1.2	7.3		
CH_4	22	999 ppmv	22	999 ppmv			22	999 ppmv	22	1001 ppmv								
H_2S	299	1.0	229	1.0	0.03	48.7	229	1.0	225	1.0	1.2	176	2.3	10.7	7.3	44.7		
COS	26	1168 ppmv	26	1168 ppmv			26	1168 ppmv	26	1170 ppmv					0.56	3.4		
CS_2	2	89 ppmv	2	89 ppmv			2	89 ppmv	2	89 ppmv								
SO_2	0.1	6 ppmv	0.1	5 ppmv			0.1	5 ppmv	0.1	5 ppmv								
$S_2O_3^=$					0.001	6.3												
$SO_3^=$					<0.0002	<1												
HCN	2.5	113 ppmv	2.5	113 ppmv	0.006	8.9	2.5	113 ppmv	0.34	16 ppmv	2.1	241	0.011	499 ppmv	2.1	12.9	<0.00001	10
HSCN					0.004	14												
NO	0.07	3 ppmv					0.07	3.2 ppmv										
NH_3	0.75	34 ppmv	0.75	34 ppmv	0.75	735												
N_2	196	0.9	196	0.9			196	0.9	196	0.9								
Ar	104	0.5	104	0.5			104	0.5	104	0.5								
Cl^-	1	50 ppmv	1	50 ppmv	1	2200												
F^-	0.06	3 ppmv	0.06	3 ppmv	0.06	66												
Methanol															0.3	1.8	0.00004	1000
Total Dry Gas	22019		22019				22018		21979				22		16			
H_2O	964		964		964				9		13227		0.3				0.07	
Total: kmol/hr kg/hr	22982 516351		22982 516349		967 17454		22016 498898		21988 497444		13242 238884		22 951		16 524		0.07 1.3	
Temperature (K)	300				300		420		280		280		280		310		310	
Pressure (MPa)	0.1				0.1		3		3		0.1		0.1		0.2		0.1	

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*The number of significant figures shown in some cases do not represent the degree of accuracy and are retained for material balance purposes only. Nevertheless, slight imbalances do appear as a result of numerical rounding. Material flow estimates and stream compositions are based upon published data and engineering estimates. Tabulated data are based upon References 7 and 24.

†Streams 215 and 214a exist only in the water-based cyanide wash case.

‡Streams 213 and 214b exist only in the methanol-based cyanide wash case.

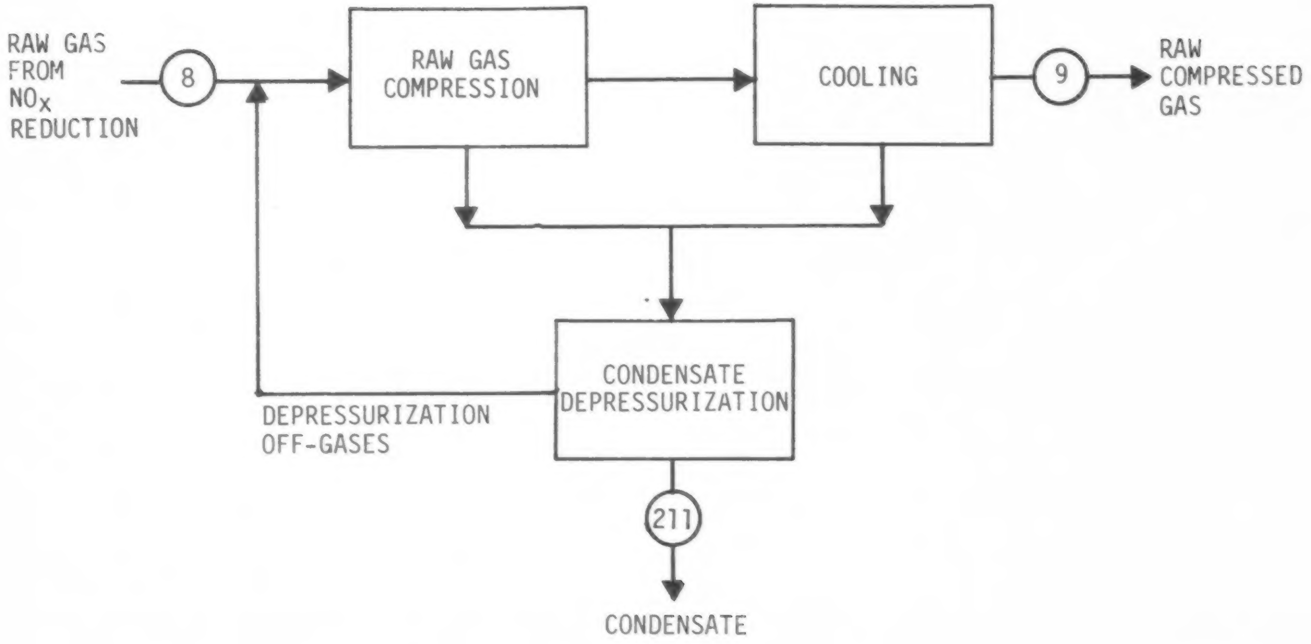


Figure 3-7. Raw gas compression and cooling

condensate depressurization offgases. Characterization data are not available for condensate depressurization offgases; however, these offgases are recycled back to the primary compression feed gas and are not a discharge stream.

Raw Gas Compression and Cooling Condensate (Stream 211)

Characterization data for raw gas compression and cooling condensate available from the K-T coal gasification facility operated by AECI Limited at Modderfontein, Republic of South Africa, are summarized in Table 3-12. These data relate to gasification of South African sub-bituminous coal and are likely to be somewhat coal specific. Material balances of the Modderfontein data indicate that virtually all of the compression feed gas ammonia was recovered in the compression condensate, while only 1 to 2% of the cyanide was recovered as either cyanide or thiocyanate. Because raw gas ammonia and cyanide levels are anticipated to be similar for bituminous and sub-bituminous coals, the quality of condensate with respect to these species is also expected to be similar.

The higher raw gas sulfide levels presented in the base case design as compared with the Modderfontein data may result in higher sulfide levels in the pressurized condensate, although depressurized condensate sulfide levels are expected to be similar. It should be noted that higher sulfide levels in the pressurized condensate could influence the levels of nonvolatile sulfur species in the condensate (e.g., SCN^-, $S_2O_3^=$, $SO_3^=$, and $SO_4^=$), provided that formation reactions for the nonvolatile sulfur species are rapid. If these reactions occur slowly, that is, occur after condensate decompression, the tabulated levels of nonvolatile sulfur species would be appropriate for the Illinois coal case. In any event, the condensate characterization data from Modderfontein provide a good qualitative basis for estimating condensate characteristics for systems utilizing other coals.

TABLE 3-12. CHARACTERISTICS OF PRIMARY COMPRESSION AND COOLING CONDENSATE FROM SOUTH AFRICAN SUB-BITUMINOUS COAL (24)

pH	8.0 - 8.2
Total suspended solids, mg/L	0 - 12
Total dissolved solids, mg/L	170 - 260
Hardness, mg/L	46 - 60
Alkalinity, p-value (as $CaCO_3$ mg/L)	0
m-value (as $CaCO_3$ mg/L)	2690 - 2990
COD, mg/L	569 - 644
NH_3, mg/L	900 - 973
CN^-, mg/L	7.2 - 10.5
SCN^-, mg/L	10.9 - 17.1
H_2S, mg/L	43.9 - 53.5
$S_2O_3^=$, mg/L	4.8 - 7.8
$SO_3^=$, mg/L	<1
$SO_4^=$, mg/L	49 - 56
PO_4^{-3}, mg/L	2 - 3

3.3.4 Cyanide Wash

Because the base plant design includes the Rectisol process for acid gas removal, minor gas constituents such as ammonia and hydrogen cyanide can complicate operation of the acid gas removal unit. Ammonia and hydrogen cyanide, which are very soluble in methanol, make methanol regeneration more complex and result in additional steam requirements (35). These contaminants may be removed from the raw compressed gas by employing a prewash of either water or cold methanol. A water wash unit is employed at the Modderfontein facility (24), and wash water to gas ratios from this unit provided the basis for the water wash system presented herein. Methanol-based cyanide wash units have been employed in several applications (partial oxidation of oil) and may be attractive for coal conversion applications where water consumption is a major concern or to minimize cyanic wastewater generation.

In the case of a water-based cyanide wash, cyanide is absorbed at 280K and 3 MPa. The rich wash water is subsequently flashed to atmospheric pressure yielding depressurized wash water (Stream 215) and sour flash gas (Stream 214a) waste streams. The depressurized cyanide wash water can be partially recycled as gasifier quench water, combined with wastewaters from the gas cooling and dust removal and raw gas compression and cooling processes and sent to wastewater treatment, or treated separately. The sour flash gas is processed through the sulfur removal/recovery system since its sulfide content corresponds to approximately 1% of the total sulfur in the gasified coal.

In the case of a methanol-based cyanide wash, cyanide absorption was assumed to proceed at 270K and 3 MPa. The rich methanol is regenerated by depressurization and indirect heating to yield a sour flash gas (Stream 214b). The sour flash gas is processed through the sulfur removal/recovery system since its sulfide content corresponds to approximately 3% of the total sulfur in the gasified coal. Because of the rigorous hot regeneration required to liberate the highly soluble cyanide from wash methanol, solvent losses with the flash gas are anticipated to be relatively high, although no operating data are available.

An additional waste stream associated with the methanol-based cyanide wash is an aqueous cyanide wash still bottoms (Stream 213). Feed gas to the cyanide wash unit contains moisture which would accumulate in the wash methanol. This moisture is recovered by distillation of the regenerated methanol.

The composition of the compressed gas after cyanide wash (Stream 10) is essentially independent of the cyanide wash absorbent used since, in either case, only a small quantity of gas is absorbed in the cyanide washer. Therefore, material flows in operations downstream of the cyanide washer (i.e., shift conversion, acid gas removal, and liquid product synthesis) are essentially independent of the cyanide wash absorbent used. For these reasons, material flow estimates for downstream operations will be provided only for the water-based cyanide wash case.

Estimated characteristics and material flows of waste streams from the cyanide wash process have been presented in Table 3-11.

Cyanide Wash Water (Stream 215)

The cyanide wash water stream exists only in the case of a water-based cyanide wash system. No characterization data are available for this waste stream. Therefore, the wash water quality has been estimated using gas solubility data (25,36). Publicly available data indicate that low pressure aqueous wash systems approach Henry's Law equilibria for HCN and NH_3 when the influence of pH is considered (7,25). Therefore, theoretical HCN and NH_3 solubility data were utilized in conjunction with absorption/desorption estimates. However, H_2S absorption does not appear to be equilibrium controlled and, therefore, empirical absorption data were utilized (7,25). Some CO_2 is also absorbed in aqueous wash systems and theoretical solubility data were used for purposes of analysis (this approach may overestimate the quantity of CO_2 in the flash gas). These estimates indicate a depressurized cyanide wash water containing 2111 mg/L CO_2, 241 mg/L HCN, and 176 mg/L H_2S. The flow rate of depressurized cyanide wash water has been factored from nominal Modderfontein operating data (24) and is approximately 238 m^3/hr.

Sour Gas from Cyanide Wash Flash - Water Wash Case (Stream 214a)

No flow rate or characterization data are available for sour flash gas from cyanide wash water depressurization. The sour gas flow rate and composition have been estimated using gas solubility data. Sour flash gas will be generated at a rate of approximately 22 kmol/hr and is composed of 89% CO_2, 11% H_2S, and 499 ppmv HCN. The sulfur content of this sour gas, 2.35 kmol/hr, corresponds to nearly 1% of the total sulfur in the gasified coal.

Sour Gas from Cyanide Wash Flash - Methanol Wash Case (Stream 214b)

No flow rate or characterization data are available for sour flash gas from cyanide wash methanol regeneration. The sour gas flow rate and composition have been estimated using gas solubility data (37). The methanol content of the sour gas has been derived from Rectisol operating data on the basis of inorganic gases stripped during hot regeneration (38). Sour flash gas will be generated at a rate of approximately 16 kmol/hr and is composed of 45% H_2S, 27% CO, 13% HCN, 7% CO_2, 3% COS, 3% H_2, and 2% methanol. The sulfur content of this sour gas, 7.3 kmol/hr, corresponds to nearly 3% of the total sulfur in the gasified coal.

Losses of H_2 and CO in this stream are expected to be small owing to their low solubility in methanol and the low methanol circulation rate required for cyanide removal. Carbon dioxide losses in this stream are small due to the low CO_2 partial pressure prior to shift conversion. Thus, the losses of H_2, CO, and CO_2 in the sour gas correspond to only 0.008%, 0.03% and 0.06% of their respective feed rates into the cyanide wash unit.

Cyanide Wash Still Bottoms - Methanol Wash Case (Stream 213)

Raw compressed gas contains a small amount of moisture which will be removed during cyanide washing by absorption in methanol. This moisture is recovered by distillation of regenerated methanol and will have a flow rate of approximately 0.001 m^3/hr. No characterization data are available for the aqueous cyanide wash still bottoms. However, HCN and methanol levels of 10 mg/L and 1000 mg/L, respectively, have been estimated as upper limit concentrations based upon data for Rectisol still bottoms at Sasol (39).

3.3.5 Shift Conversion

Methanol synthesis and hydrocarbon production via Fischer-Tropsch (F-T) synthesis can be represented by the following reactions:

$$CO + 2H_2 \xrightarrow{\text{CATALYST}} CH_3OH + \text{heat (Methanol Synthesis)}$$

$$nCO + (2n + .5x)H_2 \xrightarrow{\text{CATALYST}} C_nH_{2n+x} + nH_2O + \text{heat (F-T Synthesis)}$$

where n ranges from 1 to 20 and x = 2 for parafins and x = 0 for olefins. Since feed gas to synthesis would usually contain small amounts of CO_2 in addition to CO and H_2, and synthesis catalysts are also active for the interconnecting water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$), the hydrogenation of CO_2 may be represented as follows:

$$CO_2 + 3H_2 \xrightarrow{\text{CATALYST}} CH_3OH + H_2O + \text{heat (Methanol Synthesis)}$$

$$nCO_2 + (3n + .5x)H_2 \xrightarrow{\text{CATALYST}} = C_nH_{2n+x} + 2nH_2O \text{ (F-T Synthesis)}$$

Although the theoretical stoichiometry for synthetic liquids production calls for a ratio of 2 moles of H_2 per mole of CO and 3 moles of H_2 per mole of CO_2, in practice a stoichiometric excess of about 3% is required (1). That is:

$$H_2/(2CO + 3CO_2) = 1.03$$

Assuming a residual CO_2 concentration of about 3% in the synthesis gas, an H_2 to CO mole ratio of about 2.4:1 is required in the synthesis gas. The H_2 to CO ratio in compressed, raw K-T gas typically ranges from 1:2 to 1:2.5 (7,8,24,29), well below the ratio required for liquids synthesis. Thus, a shift conversion step is a necessary part of the gas upgrading operations for K-T based indirect liquefaction plants.

The shift conversion reaction, reaction of CO and water vapor to form H_2 and CO_2, is a mildly exothermic reaction which can be promoted by a variety of catalysts:

$$CO + H_2O = CO_2 + H_2 + 41.2 \text{ kJ/mol}$$

Shift conversion catalysts currently in use include iron-chromium, copper-zinc, and cobalt-molybdenum catalysts. Iron-chromium catalysts are active at 600K to 823K, and retain their activity and physical strength with sulfur species concentrations of up to about 200 ppmv in the shift gas (40,41,42). Copper-zinc catalysts are active at low temperatures (475K to 520K) and are typically used for final CO conversion following high temperature shift conversion. Copper-zinc shift catalysts lose activity due to poisoning by sulfur and chlorine compounds in the process gas at concentrations in the range of 1 ppmv (40,41). The newest types of shift catalysts (cobalt-molybdenum catalysts) maintain high activity over a wide range of temperatures (473K to 810K) and are not affected by the presence of gaseous sulfur compounds. Indeed, since cobalt-molybdenum catalysts are active in the sulfided form, some hydrogen sulfide is required in the process gas to maintain catalyst activity (43,44). Thus, iron-chromium or copper-zinc catalysts are applicable if shift conversion is preceded by a sulfur removal process, while a cobalt-molybdenum catalyst would be required if shift conversion precedes acid gas removal.

The sequence in which shift conversion and acid gas removal are performed is dependent upon a variety of design considerations including raw gas temperatures, acid gas removal selectivity requirements, and catalyst costs. K-T based coal conversion facilities have, in the past, employed a shift conversion process which follows raw gas sulfur removal and precedes carbon dioxide removal (e.g., the AECI Modderfontein facility). Such a configuration facilitates achievement of highly selective sulfur recovery due to the favorable H_2S to CO_2 ratio prior to shift conversion. In addition, conventional iron-chromium or copper-zinc shift conversion catalysts can be utilized. All commercial K-T coal gasification facilities utilize this configuration and the only K-T-based indirect liquefaction facility proposed in the U.S. (The North Alabama Coal Gasification Consortium Project) is expected to utilize this configuration also. This is, therefore, the approach which has been incorporated into the base plant design. Because shift conversion feed gas is the outlet gas from H_2S removal and the shift conversion outlet gas is the inlet to CO_2 removal, material flow estimates for shift conversion are presented in the acid gas removal section (Section 3.3.6).

It should be noted that an additional gas compression step will likely precede shift conversion (24). In contrast with raw gas compression, the desulfurized gas is dry and hence no compression condensate results. Since there would be no waste streams associated with this additional compression, this process is not further considered in this manual.

To achieve the required H_2 to CO ratio of about 2:1 using catalytic shifting, two approaches are possible: (1) processing the entire raw gas stream through a relatively low conversion efficiency reactor, and (2) processing a portion of the raw gas stream through a higher conversion efficiency reactor and combining the shifted and unshifted (bypass) gases afterward. Based on actual operating experience, a residual CO concentration of less than 3% can be obtained at 500K to 700K. Taking advantage of the high conversion efficiency achievable, the split flow approach is preferred since it provides costs savings associated with a smaller conversion reactor size and a smaller CO_2 absorber. A tradeoff exists between bypass fraction and degree of shift conversion. The exact bypass for a given facility is an important consideration from a cost and process efficiency standpoint. For analysis purposes, a bypass fraction of 20% has been assumed, a value which is consistent with a single stage of shift conversion. In the extreme, two stage shift conversion providing a 3% (or less) CO residual in the shifted gas would enable a bypass fraction of about one-third. The magnitude of the bypass fraction has essentially no impact upon waste stream generation in the shift section. The shift conversion operation is presented schematically in Figure 3-8.

Two waste streams associated with the shift conversion unit are spent shift catalyst (Stream 217) and shift condensate blowdown (Stream 218). Spent catalyst, in this case iron-chromium and/or copper-zinc, can either be disposed of or reclaimed, depending upon the current metal cost and reclamation trends. Shift condensate blowdown is suitable for reuse within the plant since it is low in dissolved solids although it may contain traces of ammonia and methanol from acid gas removal.

Spent Shift Conversion Catalyst (Stream 217)

Typically, iron-chromium shift catalyst contains about 44% iron and 6% chromium, and copper-zinc catalysts contain about 24% copper and 36% zinc (40,41,42,45). There is very little interest in the steel industry and specialized metals industry for recovery of iron or chromium from spent high-temperature shift catalysts, and this material will probably be disposed of directly. Spent chromium promoted copper-zinc catalysts are usually reclaimed for their copper content, although reclaimers have difficulty separating out the zinc and the chromium (46,47). Spent alumina promoted copper-zinc catalysts are usually reclaimed for both their copper and zinc contents (48). There are essentially no publicly available leachate data for these materials. However, few coal specific contaminants are expected to be present in spent shift catalysts since shift conversion follows sulfur removal from the raw gas. Spent shift catalyst generation rates are estimated to be approximately 70 Mg every 3 to 5 years.

Shift Condensate Blowdown (Stream 218)

Because shift conversion is preceded by cyanide wash and sulfur removal operations, shift condensate is expected to be free of contaminants associated with coal gasification. However, traces of methanol volatilized from the sulfur removal operation and ammonia used for pH control may be present in

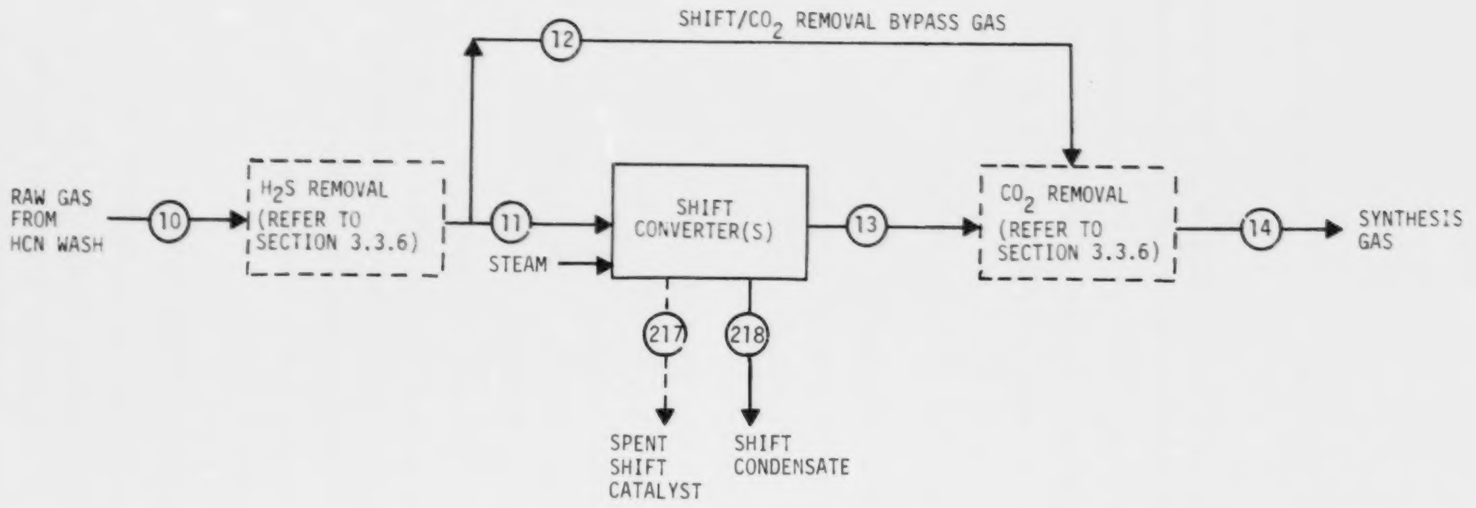

SHIFT/CO_2 REMOVAL BYPASS GAS
RAW GAS FROM HCN WASH
10
H_2S REMOVAL (REFER TO SECTION 3.3.6)
11
12
STEAM
SHIFT CONVERTER(S)
13
217
218
SPENT SHIFT CATALYST
SHIFT CONDENSATE
CO_2 REMOVAL (REFER TO SECTION 3.3.6)
14
SYNTHESIS GAS

Figure 3-8. Shift conversion

the condensate. A shift condensate blowdown is generated to control buildup on dissolved solids in the condensate recycle system. Shift condensate blowdown will be generated at a rate of approximately 3 m^3/hr. Ordinarily this very small volume waste stream would be used as makeup to the raw gas wash circuit. Hence, this stream is not considered further as a separate waste.

3.3.6 Acid Gas Removal

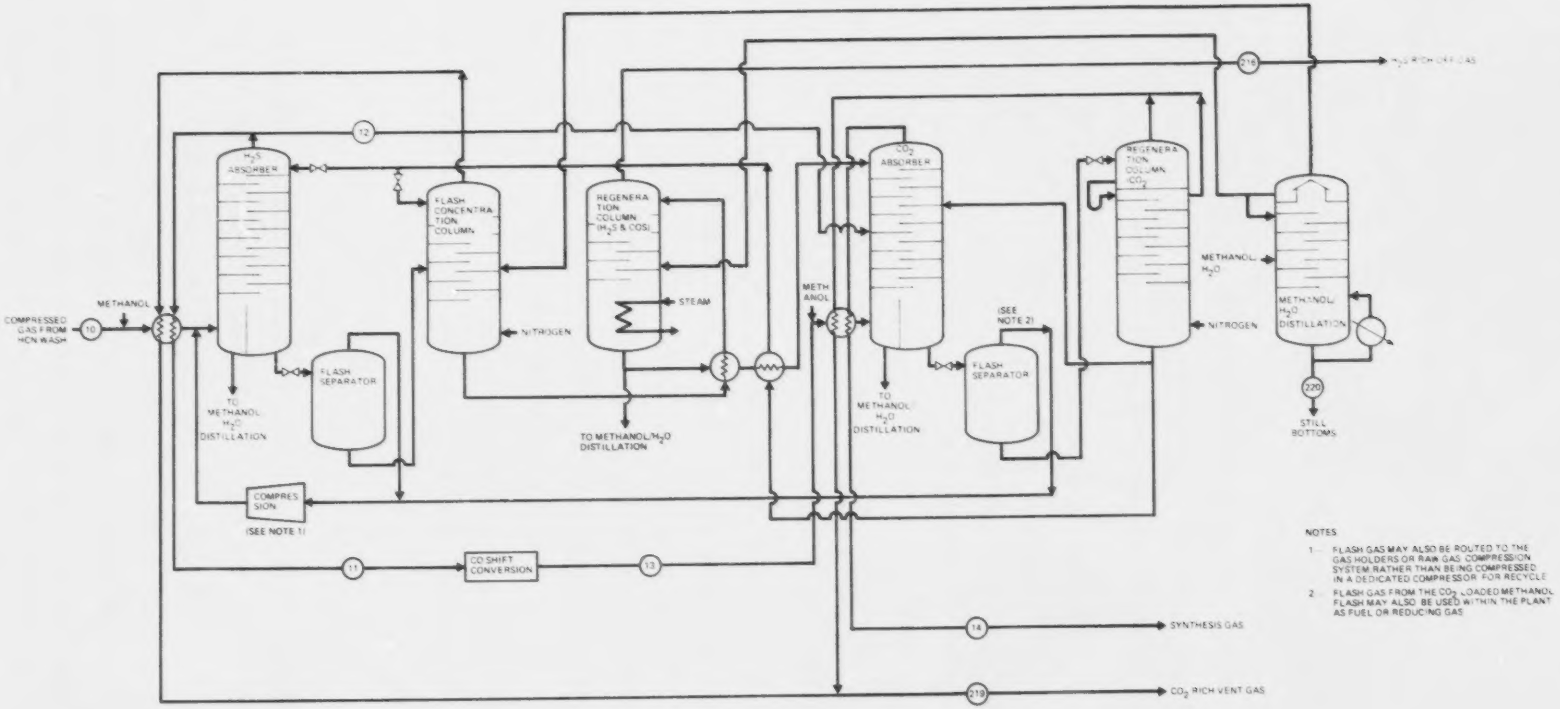
Removal of hydrogen sulfide and other sulfur compounds present in the raw K-T gas is necessary to prevent catalyst poisoning in subsequent shift conversion (if sulfur sensitive catalysts are to be used) and methanol or Fischer-Tropsch synthesis operations. Bulk removal of carbon dioxide is necessary to obtain a composition meeting the stoichiometric requirements for synthesis feed gas (see Section 3.4). There are several acid gas removal processes which have been demonstrated in coal gasification applications or similar applications. However, only the two-stage selective Rectisol process has been included in the base plant design since most of the recently commissioned K-T coal gasification facilities utilize two-stage selective Rectisol units and the only K-T based indirect liquefaction facility proposed in the U.S. is also expected to use this process. A detailed description of the Rectisol process and a summary of published performance data are presented in Appendix B and Control Technology Appendices.

Rectisol is an acid gas removal process which removes CO_2, H_2S, COS, HCN, NH_3, organic sulfur compounds, benzene, and gum-forming hydrocarbons from synthesis gases by means of physical absorption in cold methanol. The principle of operation is based upon the fact that these compounds, particularly the reduced sulfur species and CO_2, are very soluble at high pressure in cold methanol and are readily recoverable by flash desorption. Solubility coefficients (the ratios of solubility to partial pressure) of H_2S and CO_2 are higher than those of major product gases such as H_2 and CO and increase substantially with decreasing temperature while those of major product gases are relatively temperature independent. For this reason, Rectisol absorption columns operate at low temperatures, typically in the range of 210 to 250K (37,49,50). Low temperature operation also reduces solvent losses by reducing the partial pressure of methanol in the outlet streams.

Because the solubilities of reduced sulfur species (e.g., H_2S and COS) in methanol are substantially greater than that of CO_2 at the same partial pressure, the Rectisol process is capable of selective recovery of reduced sulfur species versus CO_2; to some degree, this holds for all physical absorption solvents capable of absorbing reduced sulfur species and CO_2 almost independently.

The two-stage selective Rectisol process is presented schematically in Figure 3-9. In general, a small quantity of methanol is added to the raw gas exiting the HCN washing step prior to cooling and H_2S absorption, to prevent icing. This step would not be required when a methanol-based cyanide wash process is employed. Moisture in the feed gas is removed from the H_2S absorber in solution with methanol which is recovered by distillation. Hydrogen sulfide and COS are absorbed from the feed gas using lean methanol from the CO_2 regeneration column. Rich methanol from the H_2S absorber is flashed to liberate absorbed CO and H_2 which is returned to the raw gas. Additional flashing and stripping in the concentration column, with reabsorption of reduced sulfur species in lean methanol, produces an H_2S-rich methanol stream for hot regeneration and a CO_2 offgas. Hydrogen sulfide is recovered by stripping with methanol vapor in the hot regeneration column.

Carbon dioxide is removed from shifted process gas by absorption in regenerated methanol. A small quantity of methanol is added to the shift gas prior to cooling and CO_2 absorption to prevent icing, and moisture in the shift gas is removed from the CO_2 absorber in solution with methanol. Shift conversion bypass gas may be injected into the upper portion of the CO_2 absorber. This serves as a convenient mixing point for shifted and bypass



NOTES

1 — FLASH GAS MAY ALSO BE ROUTED TO THE GAS HOLDERS OR RAW GAS COMPRESSION SYSTEM RATHER THAN BEING COMPRESSED IN A DEDICATED COMPRESSOR FOR RECYCLE

2 — FLASH GAS FROM THE CO_2 LOADED METHANOL FLASH MAY ALSO BE USED WITHIN THE PLANT AS FUEL OR REDUCING GAS

Figure 3-9. Two-stage selective Rectisol acid gas removal system

gas streams, and provides for trace sulfur removal from the bypass gas. Rich methanol from the CO_2 absorber is flashed to recover absorbed H_2. Carbon dioxide is recovered by flashing and stripping with N_2 in the CO_2 regeneration column. Material flow estimates for the shift conversion and acid gas removal operations are presented in Table 3-13.

It should be noted that desulfurization prior to shift conversion enables the use of conventional shift catalysts (e.g., iron-chromium and copper-zinc). Also, due to the favorable H_2S to CO_2 ratio before shift conversion, it facilitates production of an H_2S-rich offgas for economic sulfur recovery. Shift conversion prior to acid gas removal would result in an increased concentration of CO_2 in the H_2S absorber feed gas; the associated decrease in the H_2S to CO_2 ratio is much less favorable for highly selective operation.

There are two gaseous waste streams and one liquid waste stream produced by the selective Rectisol unit. The gaseous waste streams are the H_2S-rich offgas (Stream 216) which contains most of the sulfur present in the feed coal to gasification and the CO_2-rich offgas (Stream 219). The H_2S-rich offgas is combined with flash gas from the HCN wash and sent to sulfur removal/recovery because of its high sulfur content, while the CO_2-rich offgas is typically vented directly to the atmosphere. The liquid waste stream is the Rectisol condensate/still bottoms (Stream 220) from the methanol/water distillation column.

H_2S-Rich Offgas (Stream 216)

Approximately 94% of the total sulfur present in the feed coal to gasification is present in the H_2S-rich offgas. The offgas is estimated to contain about 50% CO_2, 42% H_2S, 5% COS, 0.4% CS_2, 340 ppmv HCN, and 200 ppmv SO_2. The only organic compound present in significant quantities is expected to be process methanol. Data indicating the total methanol loss for selective Rectisol systems are available (35,38), although data relating to methanol losses in individual streams have not been published. Therefore,

TABLE 3-13. MATERIAL FLOW ESTIMATES FOR K-T SHIFT CONVERSION AND ACID GAS REMOVAL PROCESSES (ILLINOIS NO. 6 COAL)*†

	Compressed Gas from HCN Wash Stream 10		H_2S Rich Offgas Stream 216		Shift Conversion Bypass Gas Stream 12		Shift Conversion Feed Gas Stream 11		Shift Gas to CO_2 Absorber Stream 13		Shift Condensate Stream 218	Nitrogen Strip Gas Stream 15	CO_2-Rich Vent Gas Stream 219		Rectisol Condensate/ Still Bottoms Stream 220		Combined Synthesis Gas Stream 14	
	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	kmol/hr	kmol/hr	Vol %	kmol/hr	mg/L	kmol/hr	Vol %
H_2	5829	26.5			1039	26.9	4790	26.9	12670	49.4			45	0.5			13664	67.2
CO	13699	62.3			2443	63.3		63.3	3377	13.2			101	1.0			5719	28.1
CO_2	1873	8.5	269	50.2	321	8.3	1480	8.3	9359	36.5			8875	88.2			610	3.0
CH_4	22	0.1			3.9	0.1	18	0.1	18	700 ppmv			1.2	122 ppmv			21	0.1
H_2S	225	1.0	225	42.1	0.004	1 ppmv	0.02	1 ppmv	0.02	0.8 ppmv			0.05	5 ppmv			0.02	1 ppmv
COS	26	1170 ppmv	26	4.8									0.03	8 ppmv				
CS_2	2	89 ppmv	2	0.37														
SO_2	0.1	5 ppmv	0.1	216 ppmv														
HCN	0.34	16 ppmv	0.34	636 ppmv											0.0004	10‡		
NH_3																		
N_2	196	0.9	6	1.2	35	0.9	161	0.9	161	0.6	Trace	1054	1041.	10.3			203	1.0
Ar	104	0.5			18	0.5	85	0.5	85	0.3							104	0.5
Methanol			7	1.3	Trace		Trace		Trace		Trace				0.04	1000		
Total Dry Gas	21979		535		3860		17791		25671			1054	10064				20320	
H_2O	9								55		167				64			
Total: kmol/hr	21988		535		3860		17791		25726		167	1054	10064		64		20320	
kg/hr	497444		21671		86421		398279		541238		3000	29534	422684		1160		224718	
Temperature (K)	280		310		305		305		310		370	310	305		340		305	
Pressure (MPa)	3		0.3		3		3		3		0.1	0.4	0.1		0.1		3	

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*The number of significant figures shown in some cases do not represent the degree of accuracy and are retained for material balance purposes only. Nevertheless, slight imbalances do appear as a result of numerical rounding. Material flow estimates are based upon published data and engineering estimates. Tabulated data are based upon References 7, 24, 35, 37, 38 and 39.

†A two-stage Rectisol acid gas removal system is used with shift conversion following sulfur removal and preceding carbon dioxide removal.

‡This value represents the total cyanide plus thiocyanate.

for evaluation purposes, the entire methanol loss has been assumed to be associated with hot regeneration, resulting in an estimated methanol concen- of about 1% in the H_2S-rich offgas. The H_2S-rich offgas will be generated at a rate of about 535 kmol/hr.

A somewhat higher level of selectivity has been incorporated into the Rectisol material flow estimates than is typically reported for existing units processing low-sulfur feed gases. Hydrogen sulfide concentrations in the H_2S-rich offgas from selective Rectisol units are generally in the 25 to 35% range for these applciations (35,37,38,51). However, these data are from facilities with Rectisol feed gas H_2S to CO_2 mole ratios ranging from about 1:18 to 1:66. Because of the relatively high sulfur content of the design Illinois No. 6 coal (3.13% sulfur, dry basis), the design feed gas H_2S to CO_2 ratio is about 1:8. Thus, other variables being equal, a higher selectivity would be expected. In any case, the available data indicate that H_2S concentrations of at least 25 to 35% can be obtained for a wide range of feed coal sulfur contents.

CO_2-Rich Offgas (Stream 219)

CO_2-rich offgas is generated in the subject facility at about 10,000 kmol/hr and consists of 88% CO_2 with the remainder being largely N_2. Small amounts of H_2, CO, methanol vapor, and sulfur compounds will also be present in the offgas. The CO level in the CO_2-rich offgas is related to the CO level in the shifted gas. The design in this manual is consistent with single stage shift conversion. This results in a higher level of CO in the shifted gas to the CO_2 absorber as compared to multi-stage shift conversion. Thus, the estimated concentration of CO in the CO_2-rich offgas (i.e., 1% CO) is higher than published concentrations for multi-stage shift conversion systems. Published data relating to multi-stage shift conversion systems indicate CO concentrations of 0.1% to 0.4% in the CO_2-rich offgas (35,37,38). It should be recognized that CO (and H_2) could be largely recovered by flashing of the CO_2-loaded methanol from the CO_2 absorber. This flash gas could be recycled to the raw gas or used as fuel or reducing gas elsewhere in the plant. Hence, the CO content of Stream 219 as shown in Table 3-13 probably represents an extreme case.

Methanol vapor will also be present in the CO_2-rich offgases, although no data are publicly available at present to indicate the exact level of this compound. For analysis purposes all methanol losses from the Rectisol process are assumed to be associated with the H_2S-rich fraction. Some portion of this methanol will in actuality be contained in the CO_2-rich offgas and synthesis feed gas.

A few ppm each of H_2S and COS will be present in the CO_2 offgases. Data from existing facilities indicate about 5 ppmv H_2S and 8 ppmv COS. Designs for several recent selective Rectisol plants specify less than 10 ppmv total sulfur in the CO_2-rich offgas (52).

Rectisol Condensate/Still Bottoms (Stream 220)

Little characterization data are available for Rectisol condensate/still bottoms from the methanol/water distillation. Based upon data from SASOL (39), concentrations of methanol and total cyanide (cyanide and thiocyanate) in this stream are estimated to be less than 1000 mg/L and about 10 mg/L, respectively. The generation rate for this stream is estimated to be 1 m^3/hr.

3.3.7 Trace Sulfur Removal

Although the Rectisol process can routinely achieve sulfur levels well below the ppmv required to protect synthesis catalysts, a guard bed material, employed as insurance to prevent catalyst poisoning during upset or transient conditions. Zinc oxide, the most commonly proposed guard bed material, can reduce H_2S levels to below 0.01 ppmv. However, COS levels cannot be reduced below the 0.01 ppmv level. Zinc oxide beds are closed systems during routine operation, and spent material is infrequently generated. Assuming a sulfur absorption capacity of 66 g/kg ZnO, an average of about 80 Mg/yr of spent guard material (Stream 218) would require disposal (53). If the sulfur guard bed is sized for a 3-year operating life, about 230 Mg of spent guard material would require disposal every 3 years.

3.4 PRODUCT SYNTHESIS

Methanol synthesis and hydrocarbon production via Fischer-Tropsch (F-T) synthesis can be represented by the following reactions:

$$CO + 2H_2 \xrightarrow{CATALYST} CH_3OH + \text{heat (Methanol Synthesis)}$$

$$nCO + (2n + .5x)H_2 \xrightarrow{CATALYST} C_nH_{2n+x} + nH_2O + \text{heat (F-T Synthesis)}$$

where n ranges from 1 to 20 and x = 2 for parafins and x = 0 for olefins. The mix of F-T products obtained (i.e., the range of n and x values) is dependent upon several factors including the reactor design, temperature, pressure, and type of catalyst used. Since feed gas to synthesis would usually contain some CO_2 in addition to CO and H_2 and synthesis catalysts are also active for the interconnecting water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$), the hydrogenation of CO_2 may be represented as follows:

$$CO_2 + 3H_2 \xrightarrow{CATALYST} CH_3OH + H_2O + \text{heat (Methanol Synthesis)}$$

$$nCO_2 + (3n + .5x)H_2 \xrightarrow{CATALYST} = C_nH_{2n+x} + 2nH_2O \text{ (F-T Synthesis)}$$

Although the theoretical stoichiometry for synthetic liquids production calls for a ratio of 2 moles of H_2 per mole of CO and 3 moles of H_2 per mole of CO_2, in practice the following ratio is required:

$$H_2/(2CO + 3CO_2) = 1.03 \quad (1)$$

The major difference in methanol and F-T synthesis is in the catalysts used and temperatures and pressures employed. Methanol synthesis is accomplished over Cu/Zn-based catalysts at 473K and 3.5 to 7.0 MPa while F-T synthesis proceeds over iron oxide-based catalysts at 603K (fluidized bed) and 438K (fixed bed) (3).

The Mobil M-gasoline synthesis from methanol can be represented as follows:

$$nCH_3OH \xrightarrow{\text{CATALYST}} (CH_2)_n + nH_2O$$

The process employs a zeolite-based catalyst and operates at about 573K and 2.2 MPa (1).

For methanol, F-T, and Mobil M-gasoline synthesis processes, high conversions of synthesis gas are achieved only when gas recycle is employed due to performance limitations of the catalysts. Complete recycle, however, is not possible due to the buildup of nonreactive components in the system (e.g., N_2, Ar, CH_4). Thus, all synthesis processes produce a purge gas containing inerts and lost CO and H_2. Variations in process designs for synthesis reactors reflect different approaches to heat recovery, maximum syngas conversion, minimum recycle, and minimum purge. The discussions below provide some detail about the subject synthesis processes.

3.4.1 Methanol Synthesis

Methanol production is a fully commercialized technology with a number of firms offering conversion processes including Lurgi, ICI, Chem Systems, Vulcan-Cincinnati, Mitsubishi, Nissui-Topsoe, and Selas-Polimex (3). Figure 3-10 is a simplified flow diagram of the ICI process, one of the leading commercial processes. In the ICI process, compressed synthesis feed is mixed with recycle gas and heated by exchange with methanol product before entering the synthesis reactor. The bulk of the reactor feed enters the top of the reactor while a portion of the gas, which has bypassed the remaining heat exchangers, is injected at various levels in the reactor. The cooler "quench" gases serve as the main temperature control in the system. Crude

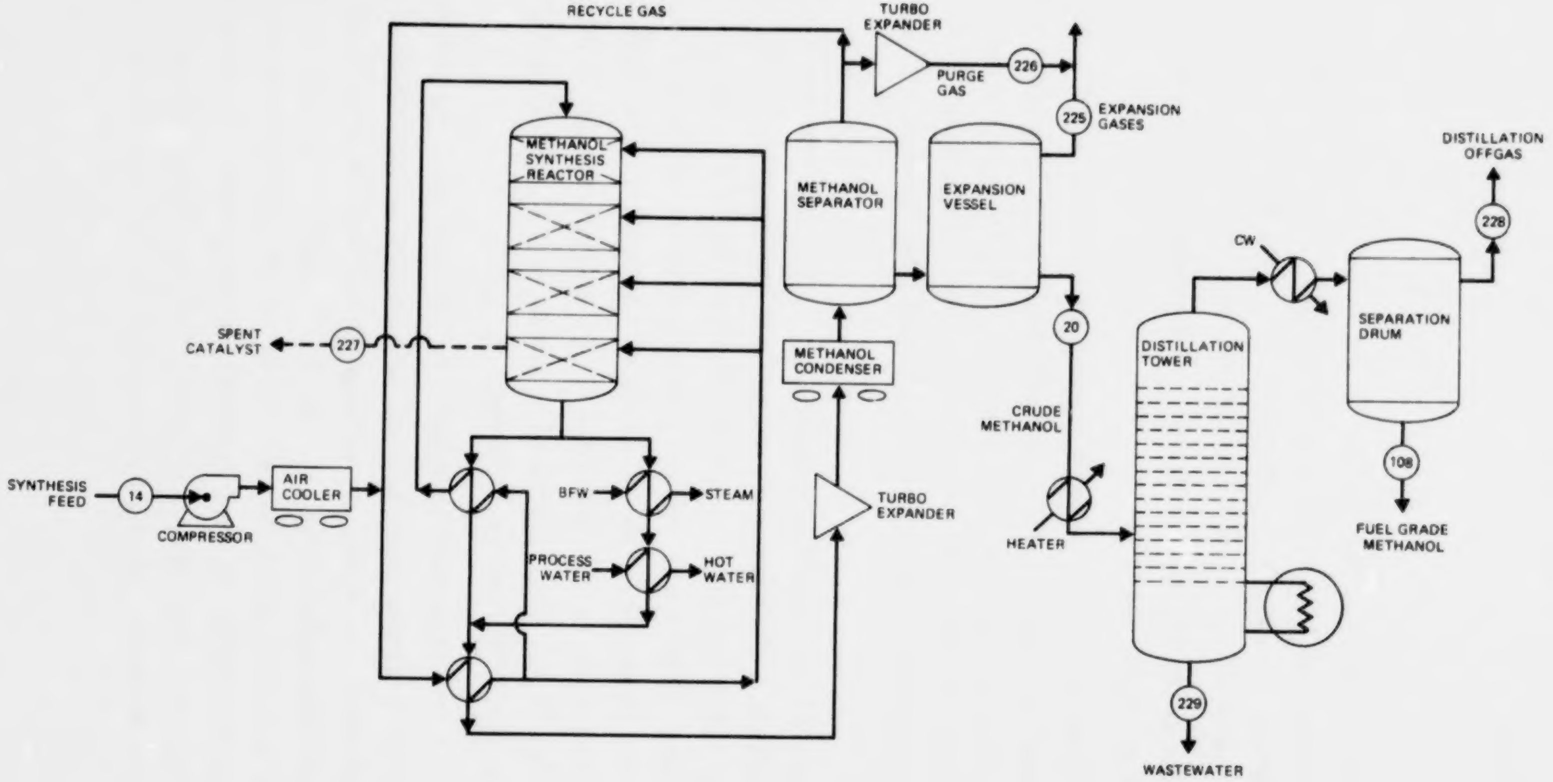

Figure 3-10. Flow diagram for the ICI methanol synthesis process

methanol vapors which exit the bottom of the reactor are cooled by feed/product heat exchange and expansion in a turbo-expander before the methanol product is condensed. Condenser overhead is partially recycled, with a purge stream withdrawn from the system through an expansion turbine. Depressurization gases from crude methanol pressure letdown are combined with these purge gases for use as plant fuel.

In the Lurgi process, a leading commercial alternative to the ICI process, the fixed bed reactor would be replaced by a boiling water jacketed tube reactor with catalyst in the tubes (1). In the Lurgi case, isothermal reactor operation is realized, and no gas quench is necessary. In all methanol synthesis processes, large amounts of heat are recovered as medium pressure steam.

Regardless of the specific process employed, all methanol synthesis processes generate a continuous purge gas and an intermittent spent catalyst. The purge gas (plus expansion and distillation gases) are useful as sulfur-free fuel gases. When crude methanol is purified by distillation, a wastewater stream is generated. The quantity of wastewater generated is almost directly proportional to the quantity of CO_2 present in the synthesis gas, and its quality (i.e., its content of methanol and higher alcohols) is dependent upon the specific process employed.

Table 3-14 presents example material flow estimates for methanol synthesis. Because a commercial facility may produce either crude methanol or fuel grade methanol, or both, estimated compositions of both crude and fuel grade methanol have been presented. As indicated by the data, a small amount of purge gas is produced due to the inerts in the synthesis feed gas. Conversion of carbon oxides to fuel methanol is about 97%. Crude methanol contains a few percent water and small quantities of higher alcohols, dimethyl ether, and low molecular weight hydrocarbons and is purified by distillation.

TABLE 3-14. METHANOL SYNTHESIS MATERIAL FLOW ESTIMATES FOR K-T GASIFICATION (ILLINOIS NO. 6 COAL)*

Constituent	Feed Gas Stream 14		Crude Methanol Stream 20		Purge Gas Stream 226		Expansion Gas Stream 225		Fuel Grade Methanol Stream 108		Wastewater Stream 229		Distillation Offgas Stream 228	
	kmol/hr	Vol %	kmol/hr	Wt %	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Wt %	kmol/hr	Wt %	kmol/hr	Vol %
CO	5719	28.1	0.02	<0.01	106	8.1	2.5	8.3	0.01	<0.01			0.003	1.0
H_2	13664	67.2	0.02	<0.01	818	62.5	7.5	25.0	0.02	<0.01			0.003	1.0
CO_2	610	3.0	1.5	0.03	58	4.4	11	36.7	1.3	0.03			0.2	62
CH_4	21	0.1	0.01	<0.01	20	1.5	0.8	2.7	0.01	<0.01			0.002	1.0
N_2 + Ar	307	1.5	0.02	<0.01	304	23.2	3.3	11.0	0.02	<0.01			0.003	1.0
CH_3OH			6123	95.1	4.0	0.3	4.6	15.3	6120	99.7	3.0	1.0	0.1	33
$(CH_3)_2O$			5.1	0.12	0.08	0.01	0.1	0.3	5.1	0.12			0.002	1.0
C_2H_5OH			1.9	0.04					1.9	0.04	0.001	<0.01		
C_3H_7OH			1.2	0.03					0.02	<0.01	1.2	0.74		
H_2O			549	4.8	0.05	0.04	0.06	0.2	11	0.1	538	98.25		
Total	20320	100	6682	100	1309	100	30	100	6139	100	542	100	0.35	100

*Material flow estimates are based upon published engineering studies (1,2).

3.4.2 Fischer-Tropsch (F-T) Synthesis

The F-T process can produce a wide range of products from methane to heavy fuel oil. Generally, fluidized bed designs operating at higher temperatures produce a lighter mix of products than fixed bed designs. For purposes of analysis, it is assumed that the fluidized bed design similar to that used at Sasol, S.A. (called the Synthol process) would be utilized in the U.S. since major emphasis in synfuels production would be on light motor fuels. However, even the Synthol process produces a range of products from middle distillates to methane. An indirect liquefaction plant using F-T synthesis could be designed to produce mostly liquid products by: (1) steam reforming of methane and other light hydrocarbons for recycle and (2) catalytic cracking of heavier oils. Such an approach, however, would result in low overall thermal efficiencies due to extensive heat losses. Thus, a mix of hydrocarbon products including SNG, LPG, gasoline, diesel fuel, alcohols, and ketones may be a more practical scenario for U.S. facilities.

Figure 3-11 is a flow diagram of the Synthol process (1). Purified synthesis gas and recycle gas are compressed together and heat exchanged against hot reactor product. Synthesis gas is mixed with circulating iron catalyst in the Synthol reactor where the synthesis reactions proceed. Reaction heat is removed by hot oil circulating in tubes internal to the reactor. Catalyst and vapor products are separated in a cyclone system and catalyst solids are recycled. Crude product vapors are cooled in a hot wash tower which uses cooled F-T recycle oil as the wash medium. Heat is recovered via feed/product exchange and by generation of steam in waste heat boilers.

Heavy oil condensate is sent to product fractionation while hot wash tower overhead is sent to a cold wash tower for recovery of lighter oils. In the cold wash tower, cool process water spray effects condensation of

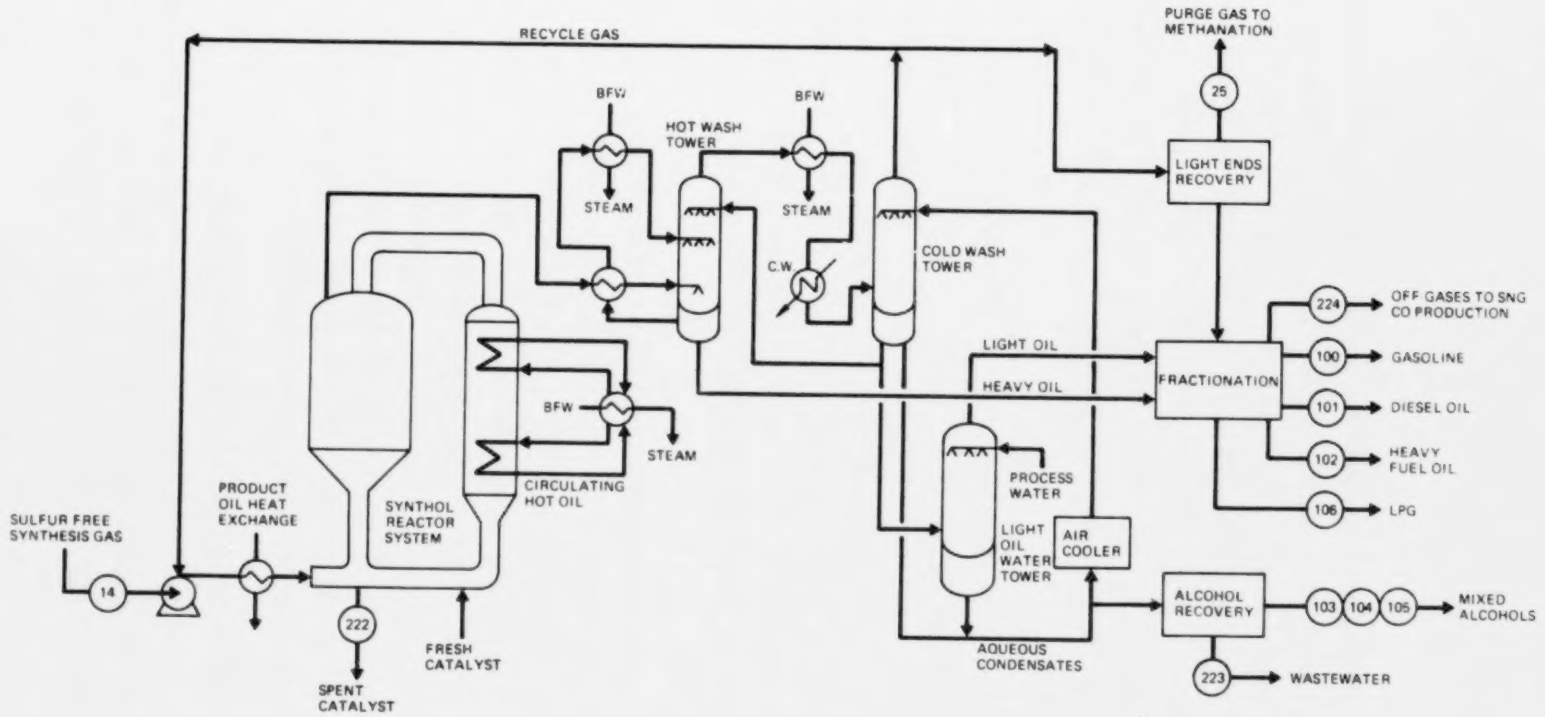

Figure 3-11. Fischer-Tropsch (Synthol) synthesis and product recovery

most of the light hydrocarbons; oxygenated organics (alcohols, ketones, acids) become dissolved in the aqueous condensate. Liquid light oil is further washed with process water and sent to product fractionation. The aqueous condensate is neutralized with lime and stripped to recover alcohols and ketones. Stripper bottoms, containing mostly organic acids, constitute the aqueous waste from the F-T process. Overhead vapors from the cold wash tower are split into a recycle and a purge stream, with the latter sent to catalytic methanation.

Not shown in Figure 3-11 is the catalyst preparation process. At Sasol, S.A., catalyst is prepared on-site from iron ore via reduction with fuel gas (39). Other transition metals are added as promotors during the preparation step. It is not known whether F-T catalyst would be prepared on-site (at least the ore reduction step) for U.S. facilities or purchased from a vendor. For simplicity, it is assumed that no preparation other than mixing/packaging would be conducted on-site and thus no wastes are generated by the preparation step.

Table 3-15 presents example material flow estimates for F-T synthesis. About 15% of the heating value of F-T products is accounted for by purge gas which is subsequently converted to SNG. Light hydrocarbons in the fractionation light gas would be recovered as LPG and a fuel gas (or as methanation feed). F-T middle oil is about 80% gasoline range hydrocarbons and 20% diesel/fuel oil hydrocarbons. Alcohols (and ketones) represent significant chemical by-product(s). A relatively large amount of wastewater is generated in the F-T process, since approximately one mole of water is produced for each mole of carbon oxides reacted during hydrocarbon synthesis.

3.4.3 Methane Co-production (Fischer-Tropsch Synthesis Case)

Purge gas from light ends recovery in the F-T synthesis case contains large amounts of methane along with CO and H_2. An efficient way to recover the fuel value of these purge gases is to convert residual hydrogen and

TABLE 3-15. FISCHER-TROPSCH SYNTHESIS MATERIAL FLOW ESTIMATES FOR K-T GASIFICATION (ILLINOIS NO. 6 COAL)*

	Feed Gas Stream 14		Purge Gases to Methanation Stream 25		Wastewater from Alcohol Recovery Stream 223		Fractionation Offgases to CO_2 Removal Stream 224		Methanation Condensate Stream 236		Wastewater from CO_2 Stream 235		CO_2 Removal Offgas Stream 239		Dehydration Offgas Stream 240		CO-Product SNG Stream 107	
	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Wt %	kmol/hr	Vol %	kmol/hr	Wt %	kmol/hr	Wt %	kmol/hr	Wt %	kmol/hr	Vol %	kmol/hr	Vol %
H_2	13664	67.2	973	30.4			5.42	1.22					0.0287	0.01			2.77	0.188
N_2 + Ar	307	1.51	307	9.57			5.17	1.17					0.794	0.291			302	20.5
CO	5719	28.1	61.4	1.92			1.18	0.267					0.0042	0.001			0.301	0.02
CO_2	610	3.00	396	12.3			139	31.4					253	92.7			131	8.94
CH_4	20.8	0.102	612	19.1			44.8	10.1					15.5	5.67			1028	69.9
H_2O			12.4	0.386	8820	98.9	12.3	2.78	703	98.1	22.9	100	3.01	1.11	10.6	100	6.35	0.432
C_2H_4			118	3.67			61.2	13.8					0.252	0.06				
C_2H_6			177	5.52			103	23.2					0.150	0.09				
C_3H_6			240	7.49			65.4	14.8					0.016	0.006				
C_3H_8			40.0	1.25			6.31	1.42					0.159	0.06				
C_4H_8			122	3.82			0.08	0.002										
C_4H_{10}			15.7	0.491			0.01	0.003										
C_5-C_7			108.88	3.402			0.03	0.006										
C_7 + oils			21.7	0.678			0.22	0.05										
Organic Acids					29	1.1			4.2	1.9								
Total kmol/hr	20320		3204		8849		443		707.2		22.9	100	273		10.6	100	1470	
Total kg/hr			78340		160600		15100		12910		413		11490		191		33240	

*Material flow estimates are based upon published engineering studies (1). Main products from Fischer-Tropsch synthesis are:

Blended gasoline (Stream 100) - 41320 kg/hr
C_3 LPG (Stream 106) - 2699 kg/hr
C_4 LPG (Stream 106) - 410 kg/hr
Diesel oil (Stream 101) - 8380 kg/hr
Heavy fuel oil (Stream 102) - 2454 kg/hr
Mixed alcohols (Streams 103,104,105) - 6995 kg/hr

carbon oxides in the gases to additional methane, producing high heating value gas equivalent to pipeline gas (substitute natural gas or SNG). Methanation involves the catalytic reaction of carbon oxides in the gases to methane as indicated by the following reactions:

$$3H_2 + CO = CH_4 + H_2O + \text{heat}$$

$$4H_2 + CO_2 = CH_4 + 2H_2O + \text{heat}$$

Figure 3-12 is a simplified flow diagram for SNG production showing catalytic methanation, CO_2 removal, and drying.

The methanation reactions which are carried out over nickel-based catalyst at 573 and 753K and 7 MPa (54) are highly exothermic. In the fixed bed design shown in Figure 3-12 temperature is controlled by recycle of cooled product gas. Also, a large amount of steam is recovered in this process. Water vapor formed during methanation is condensed in knockout drums and the condensate is subsequently depressurized for reuse as a boiler feed water. Methanator product gas is most commonly treated for CO_2 removal using an amine-based acid gas removal system (e.g., monoethanolamine). Final moisture removal is usually accomplished in a triethylene glycol (TEG) absorber.

The material flow estimates for SNG co-production have been included in Table 3-15.

Waste streams generated continuously during SNG co-production are methanation and CO_2 removal, CO_2 containing offgases, dehydration offgas, methanation catalyst, decommissioning offgases and spent methanation catalyst.

3.4.4 Mobil M-Gasoline Synthesis

The Mobil M-gasoline process is depicted in Figure 3-13 (1). Crude methanol is vaporized by heat exchange with reactor product and fed to the dimethyl ether (DME) reactor where it is catalytically converted to an

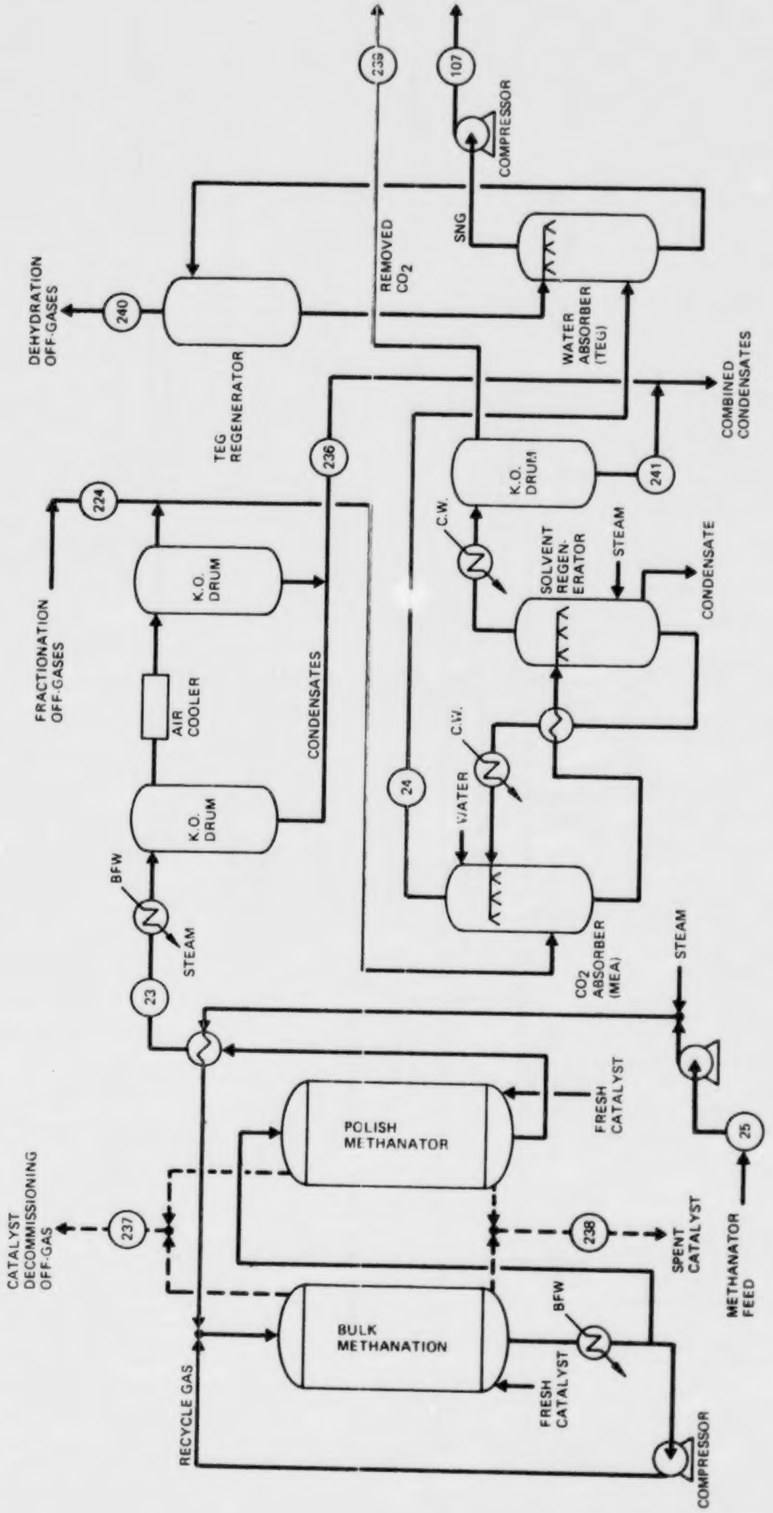

Figure 3-12. Methanation, CO_2 removal, and drying for SNG production

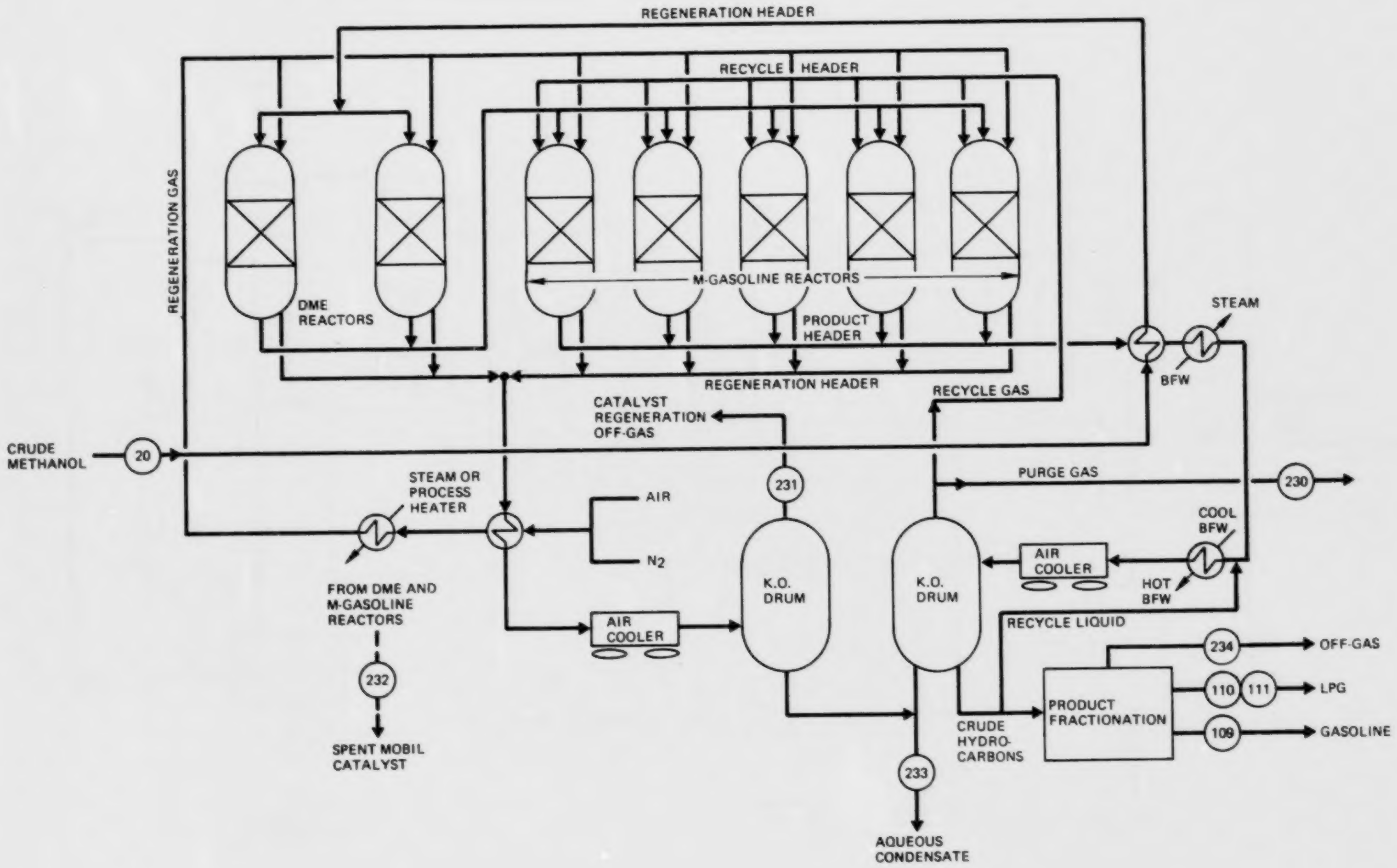

Figure 3-13. Flow diagram for Mobil M-gasoline synthesis and crude product fractionation (1)

equilibrium mixture of methanol, DME, and water vapor. DME reactor product is subsequently converted to hydrocarbons in M-gasoline reactors, with temperature control obtained by recycling cooled purge gas from product separation. The DME reactor inlet conditions are about 573K and 2.3 MPa while M-gasoline inlet conditions are 603K. Product vapors from the M-gasoline reactors are cooled by methanol feed heat exchange, by generation of steam in a waste heat boiler, and by air cooling. Crude liquid product is separated in a knockout drum. Drum overhead is split into a recycle stream and a purge stream used as plant fuel. The bulk of liquid product is sent to the product fractionation unit for light ends recovery, with a small slipstream injected at the inlet to the boiler feed water heat exchanger to control Durene* crystallization. The aqueous condensate from the knockout drum (Stream 233) constitutes the only continuous wastewater stream from the process.

Both the DME catalyst and M-gasoline catalyst require periodic regeneration. The DME catalyst accumulates coke slowly and requires regeneration perhaps once or twice per year. The M-gasoline catalyst requires regeneration about every two weeks to remove coke. Regeneration is accomplished using N_2 to purge hydrocarbons from the system followed by air injection. Control of inlet O_2 level and injection of cooled recycle gas to the system maintain combustion temperatures below 753K. Regeneration offgas is cooled by exchange with fresh regeneration gas and by air cooling. Any water of combustion is condensed in a knockout drum before depressurization and venting to the atmosphere. As depicted in Figure 3-13, five M-gasoline reactors constitute a "train" with one reactor being regenerated while four are in service. Thus, regeneration is a regular but intermittent process resulting in the routine generation of an offgas.

Table 3-16 presents example mass flow calculations for Mobil M-gasoline synthesis. As indicated in the table, a small methanol synthesis purge stream

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*1,2,4,5-tetramethylbenzene (Durene) has a very high octane rating and is desirable in product gasoline for that reason but it freezes at 353K.

TABLE 3-16. MOBIL M-GASOLINE SYNTHESIS MATERIAL FLOW ESTIMATES FOR K-T GASIFICATION (ILLINOIS NO. 6 COAL)*

Constituent	Crude Methanol Stream 20		Purge Gas Stream 226		Expansion Gas Stream 225		Crude Product Stream 21		Fuel Gas Stream 230		Condensate Stream 233	
	kmol/hr	Wt	kmol/hr	Vol	kmol/hr	Vol	kmol/hr	Vol	kmol/hr	Vol	kmol/hr	Wt
CO	0.02	<0.01	106	8.1	2.5	8.3	0.7	0.07	0.3	2.3	0.04	
H_2	0.02	<0.01	818	62.5	7.5	25.0	1.6	0.15	0.9	6.8		
N_2 + Ar	0.02	<0.01	304	23.2	3.3	11.0	0.01	0.001	0.006	0.04		
CO_2	1.5	0.03	58	4.4	11	36.7	3.5	0.33	0.3	2.6	0.68	0.03
CH_4	0.01	<0.01	20	1.5	0.8	2.7	39.0	3.7	6.8	50.8		
C_2H_4							1.0	0.10	0.06	0.5		
C_2H_6							12.6	1.2	0.6	4.3		
H_2O	549	4.8	0.05	0.004	0.06	0.2	4.2	0.4	0.2	1.6	6099	99.0
CH_3OH	6123	95.1	4.0	0.3	4.6	15.3						
$(CH_3)_2O$	5.1	0.12	0.08	0.01	0.1	0.33						
C_2H_5OH	1.9	0.04										
C_3H_7OH	1.2	0.03										
C_3H_6							3.9	0.36	0.08	0.6		
C_3H_8							89.0	8.4	1.6	11.6		
i C_4H_{10}							131.2	12.4	1.2	8.7		
C_4H_8							16.4	1.6	0.1	1.0		
n C_4H_{10}							40.6	3.8	0.3	2.1		
i C_5H_{12}							144.0	13.6	0.5	3.7		
C_5H_{10}							26.6	2.5	0.09	0.7		
n C_5H_{12}							16.4	1.5	0.05	0.4		
C_6^+							531	50.0	0.3	2.5	1.35	0.10
C_3H_6O											7.92	0.42
CH_2O_2											10.0	0.42
Coke												
Total moles	6682	100	1309	100	30	100	1061	100	13.4	100	6119	100

*Material flow estimates are based upon published engineering studies (1).

is produced which accounts for less than 10% of the total product heating value. Most of the remaining fuel value is recovered as gasoline and LPG. Mobil M-gasoline offgas and fractionation light gas are used as plant fuels. The aqueous condensate waste (Stream 233) contains the oxygenated organics (ketones, acids) which are generated in small amounts in the Mobil M-gasoline catalytic reactors.

3.4.5 Product Recovery and Upgrading

The crude liquid fuel products of methanol, F-T, and Mobil M-gasoline syntheses may require upgrading on-site to yield final products which are marketable as substitutes for petroleum-derived fuels and chemicals. This is particularly true for motor gasolines, where crude coal-derived gasoline fractions would not meet octane requirements for the retail market in the U.S. F-T and Mobil M-gasoline products could be upgraded by catalytic alkylation of the C_3-C_4 fraction to yield gasoline-blend hydrocarbons and commercial grade LPG, by hydrotreating (in the F-T case for destruction of olefins and oxygenated organics), by catalytic reforming to produce more cyclic and branched chain hydrocarbons, by C_5/C_6 isomerization to increase the antiknock quality of pentanes and hexanes, and by catalytic polymerization to convert propene/butene fractions into higher molecular weight gasoline blending compounds. All of these upgrading processes are standard refinery technology. Further, waste streams generated during upgrading (e.g., alkylation sludges, condensates) are not expected to present treatment problems other than those encountered in existing refineries since feed streams to upgrading processes have no unique characteristics differing from current refinery experience. In fact, the absence of sulfur and nitrogen in the synthesis products elminates waste streams such as sour waters and gases often generated in the upgrading of petroleum fractions. Control of refinery waste streams has been discussed in several reports (55,56,57) and therefore will not be addressed in this manual. For these reasons and due to the multiplicity of possible options for product upgrading, the "plant boundary" chosen for purposes of this manual includes only crude product separation/fractionation. The one exception to this defined plant boundary is the fugitive organic emissions inventory which includes emissions from all upgrading processes (refer to Section 3.7).

Tables presented previously in Section 3.4 have shown the characteristics and flow rates of crude synthesis products consistent with the plant boundary defined for purposes of this manual. Table 2-2 in Section 2 presented typical upgraded product slates for K-T based facilities. This mix of upgraded products is assumed in Section 3.6 for purposes of estimating evaporative emissions from product storage.

3.4.6 Waste Streams Generated by Synthesis Operations

Synthesis operations do not generate any continuous gaseous waste streams. All purge gases are valuable as sulfur-free fuels or as SNG feed. However, periodic regeneration or decommissioning of catalysts results in the generation of offgases. In addition, spent catalysts requiring disposal constitute an intermittent solid waste. Aqueous wastes are routinely generated by methanol, F-T, Mobil M-gasoline, and SNG synthesis. In all but the SNG case, these wastewaters contain oxygenated organics requiring treatment. SNG condensates contain only dissolved gases and are reusable as boiler feed water after degassing. Water produced during methanol synthesis is found in the crude methanol fuel product.

Spent Methanol Synthesis Catalyst (Stream 227)

No data are currently available in the public domain relating to the characteristics or quantity of spent methanol catalyst. For the subject facility a catalyst inventory of about 300 Mg having a useful life of 3-5 years is assumed. Therefore, based on these assumptions, the average annual spent catalyst rate is 60 to 100 Mg.

Spent F-T Catalyst (Stream 222)

As with methanol catalyst, no data are currently available on properties of spent catalyst. Further, amounts and types of metals other than iron which are used in formulations of fresh catalysts are proprietary. Based on data for the Sasol, S.A. facility, about 5200 Mg/year of spent F-T catalyst would be generated (1).

Spent Mobil M Catalyst (Stream 232)

Mobil M catalysts are zeolite-based (synthetic clay-like) materials. No data are publicly available at present on the characteristics of these catalysts. It is estimated that the subject facilities would generate about 80 Mg/year of spent DME catalyst and about 300 Mg/year of spent M-gasoline catalyst (1).

Mobil M Synthesis Catalyst Regeneration Offgas (Stream 231)

Based on design data contained in a Mobil report (1) concerning the number of catalyst vessels, regeneration frequency, regeneration duration, and offgas volume, it is anticipated that catalyst regeneration will occur over a period of about 3800 hours per year with an average offgas flow rate of approximately 4600 Nm^3/hr. Pollutants of concern in the offgas stream which may require control are VOC, carbon monoxide, and particulate matter. No data are currently available on the composition of the subject waste gases.

Spent Methanation Catalyst (Stream 238)

Nickel-based methanation catalysts are eventually deactivated by physical degradation of crystal size and by chemical accumulation of poisons such as sulfur. No data are currently available on the leachability of nickel from spent methanation catalyst. The average generation rate of spent catalyst is estimated at about 40 Mg/year.

Methanation Catalyst Decommissioning Offgas (Stream 237)

Methanation catalyst contains nickel in reduced form and is thus pyrophoric in nature. Prior to removal of spent catalyst from the bed, the material is oxidized with air in a controlled manner to convert nickel to its oxide. No information is available on the characteristics of the catalyst decommissioning offgas.

Methanol Synthesis Condensate (Stream 229)

Based on the calculations in Table 3-14, methanol synthesis condensate has the following characteristics:

Production rate	10 m^3/hr
Methanol	10,000 mg/L
Ethanol	5 mg/L
Propanol	7,400 mg/L
COD	33,000 mg/L
TOC	7,400 mg/L

The condensates will contain very low inorganic TDS levels, no sulfur or nitrogen species, and no significant levels of trace elements. The volume of this stream is determined by the CO_2 level in the feed gas which is, in turn, determined by Rectisol design. The exact composition of methanol systems condensate will vary with the specific process employed.

F-T Wastewater (Stream 223)

Condensates generated by the F-T product separation step have the following estimated characteristics (1) (see Table 3-15):

Production rate	160 m^3/hr
Organic acids	10,800 mg/L
COD	12,000 mg/L
TOC	4,300 mg/L

Although the condensates would inherently have low inorganic TDS levels, during product separation the F-T condensates are neutralized with lime or caustic to allow distillation of alcohols and ketones while leaving acids in the aqueous phase. Thus, the wastewaters would also have high levels of alkalinity and Ca^{++} or Na^{+}. No significant levels of trace elements are expected.

Mobil M-Gasoline Wastewater (Stream 233)

Condensates generated by the Mobil product separation step have the following estimated characteristics (1,2) (see Table 3-16):

Production rate	110 m^3/hr
Formic acids	4,200 mg/L
Acetone	4,200 mg/L
C_6 + hydrocarbons	1,000 mg/L
COD	14,000 mg/L
TOC	4,000 mg/L

The waste will contain very low levels of inorganic TDS, no sulfur or nitrogen compounds, and no significant levels of trace elements. The estimates for gross parameters or constituents may be lowered when chemical recovery is practiced. Also, the specific catalyst will affect condensate quality. Methanol synthesis condensate is not generated separately in Mobil M-gasoline facilities. Water produced in methanol synthesis is ultimately found in Mobil M-gasoline wastewater.

Methanation Condensate (Stream 236)

Water contained in crude SNG is condensed under pressure and contains about 10 mg/L CH_4 and 20,000 mg/L of CO_2 (58). About 12,910 kg/hr of condensate are generated. Since this stream contains essentially no dissolved solids, it is reusable as boiler feed water after depressurization and air or N_2 stripping to remove dissolved gases. In an integrated facility, methanation condensate would be considered an internal process stream rather than a waste stream.

CO_2 Offgas from SNG Purification (Stream 239)

In most cases, residual CO_2 in the methanation product (crude SNG) would be removed to obtain a pipeline quality gas. Since amine processes for CO_2 removal will also remove some CO, H_2, and hydrocarbons, the offgas will contain these constituents in the following approximate amounts (1,58):

CO_2	93 vol %
CO	15 ppmv
H_2	105 ppmv
CH_4	1 vol %
C_2H_4	550 ppmv
C_2H_6	925 ppmv
C_3H_6	582 ppmv
C_3H_8	58 ppmv
H_2O	5.8 vol %

The total flow rate is estimated to be approximately 273 kmol/hr.

Dehydration Offgas (Stream 240)

The triethylene glycol regenerator offgas contains very small amounts of methane and the glycol solvent. No data are available to quantify these constituents. The offgas flow rate is around 1000-2000 kg/hr and consists mostly of water vapor.

CO_2 Removal Wastewater (Stream 235)

The fractionation offgas sent to the CO_2 removal unit in an F-T synthesis facility is estimated to contain appreciable quantities of water. As a result, wastewaters are generated in the CO_2 removal step. The flow rate of this waste stream is estimated at approximately 400 kg/hr. Composition data are not available for this waste stream, but it should contain only minor quantities of dissolved gases such as CO_2. As such it could be combined with the methanation condensate for reuse within the facility.

3.5 PRODUCTS AND BY-PRODUCTS

The products/by-products considered in this section include those produced as substitutes for petroleum-derived fuels or chemicals and sulfur recovered as a result of air and water pollution control. The available data on the composition of each product and by-product are presented, and those substances or classes of substances which would be considered toxic are identified. However, it should be noted that product and by-product speciation data are generally limited. Data presented herein should not be construed as an adequate basis for evaluating the potential environmental risks associated with products and by-products.

3.5.1 Methanol Synthesis Product

Methanol is currently produced primarily from natural gas (59). The composition of the crude product varies somewhat depending upon such factors as the specific synthesis process used, the synthesis pressure and temperature, and the hydrogen to carbon monoxide ratio in the synthesis feed (59). The primary reaction in methanol synthesis is:

$$CO + 2H_2 \xrightarrow{\text{CATALYST}} CH_3OH + \text{heat}$$

However, a number of side reactions also take place which introduce impurities into the crude methanol product. A representative, but not exhaustive, list of impurities which can be expected in crude methanol is presented in Table 3-17. An additional, and highly toxic, potential impurity not shown in the table is iron carbonyl. Under certain conditions the formation of this compound has been observed in the compression and synthesis sections of methanol plants (60).

Table 3-18 shows an estimated composition of a crude methanol made from coal. As with a natural gas feed the amounts and types of impurities present will vary somewhat depending upon the specific synthesis process used and process conditions. However, water is expected to be the largest single impurity (5%) with all others comprising less than 1%. It should also be mentioned that several methods for purifying methanol are currently available (59), and the degree of methanol purification will largely be determined by user needs. Thus, coal-derived methanol in commerce may range in purity from about 95% pure in the case of the crude product to 99.85% pure for Grade AA methanol.

TABLE 3-17. COMPONENTS REPORTED IN COMMERCIAL METHANOL (59)

Compounds

1. Dimethyl Ether
2. Acetaldehyde
3. Methyl Formate
4. Diethyl Ether
5. n-Pentane
6. Propionaldehyde
7. Methyl Acetate
8. Acetone
9. Methanol
10. Isopropyl Ether
11. n-Hexane
12. Methyl Propionate
13. Ethanol
14. Methyl Ethyl Ketone
15. t-Butyl Alcohol
16. n-Propanol
17. n-Heptane
18. Water
19. Methyl Isopropyl Ketone
20. Acetal
21. Isobutanol
22. n-Butyl Alcohol
23. Isobutyl Ether
24. Diisopropyl Ketone
25. n-Octane
26. Isoamyl Alcohol
27. 4-Methyl Amyl Alcohol
28. n-Amyl Alcohol
29. n-Nonane
30. n-Decane

TABLE 3-18. ESTIMATED COMPOSITIONS OF CRUDE METHANOL FROM COAL* (2)

Compound	Concentration
CH_3OH	94.6%
C_2H_5OH, C_3H_7OH and C_4H_9OH	2800 ppm
$(CH_3)_2O$	150 ppm
Nonmethane HCs	600 ppm
H_2O	5.0%

*The composition of crude methanol is highly process specific. These estimates are based upon the ICI synthesis process.

3.5.2 Fischer-Tropsch Liquid Products

The crude Fischer-Tropsch synthesis product is primarily composed of straight-chained paraffinic and olefinic hydrocarbons (61). Minor quantities of aromatic, naphthenic, and branched-chain hydrocarbons are also present, along with small amounts of oxygenated compounds such as alcohols, aldehydes, ketones, and acids, most of which have fewer than five carbon atoms (62). The crude F-T product (Stream 22) can be refined into several different products including LPG (Stream 106), gasoline (Stream 100), diesel oil (Stream 101), heavy oil (Stream 102), methanol (Stream 103), acetone and methyl ethyl ketone (MEK) (Stream 104), and heavy alcohols (Stream 105). Much of the chemical composition data presented here is based on analyses of products from the commercial-scale Fischer-Tropsch synthesis plant which is currently operating in Sasolburg, South Africa.

Limited data on the composition of gasolines, diesel oils, and heavy oils from F-T synthesis indicate that they are essentially nitrogen-and-sulfur-free (63). Crude Fischer-Tropsch gasoline requires upgrading prior to its use as a motor fuel, and Table 3-19 shows the estimated chemical composition, by compound class, of the finished Fischer-Tropsch gasoline. The aromatics content (17%) is lower than that of typical petroleum gasolines (23-36%). The saturates content is similar to that of petroleum-derived gasoline, but the olefins content is much higher. The estimated Reid Vapor Pressure of 69 kPa for finished Fischer-Tropsch gasoline is within the range of values (48 to 100 kPa) for typical petroleum gasolines (64).

Table 3-20 shows the distribution of the oxygenated by-products from fluid bed Fischer-Tropsch synthesis before further refining. At the SASOL plant, the aldehydes are hydrogenated, and methanol is reported to be used onsite as Rectisol solvent makeup. Ethanol, propanol, butanol, pentanol, acetone, MEK, and a higher alcohol fraction are distributed commercially (63). The SASOL operators also convert the propylene and butylene from the light ends recovery to gasoline by polymerization over a solid phosphoric acid catalyst. The propane and butane are sold as LPG (65).

3.5.3 Mobil M-Gasoline Products

The crude Mobil M-gasoline synthesis product (Stream 21) is fractionated into a gasoline (Stream 109), mixed butanes (Stream 110) and propane (Stream 111). Table 3-21 which shows the expected composition of the synthesis product, representing an average yield over 14 days of operation before catalyst regeneration (1).

Table 3-19 presented the estimated composition of the crude Mobil M-gasoline. It can be seen from this table that the olefins content of the Mobil M-gasoline is higher than that of petroleum gasoline, while the saturates and aromatics contents are within the ranges found in petroleum gasolines. The benzene content of the finished Mobil M-Gasoline is also reported to be less than the one percent by volume which is typical of petroleum gasolines (64). As was mentioned earlier, iron carbonyl could be present in trace quantities in the methanol feed. It is, however, expected that any

TABLE 3-19. COMPARISON OF THE ESTIMATED COMPOSITION OF FINISHED INDIRECT COAL LIQUEFACTION, UNLEADED GASOLINES, AND TYPICAL PETROLEUM GASOLINES

Component	Fischer-Tropsch Unleaded Gasoline (Refs. 1,63)	Finished Unleaded Mobil M-Gasoline (Ref. 1)	Crude Mobil M-Gasoline (Ref. 1)	Petroleum-Derived Gasolines (Refs. 66,67,68)
Saturates, vol %	63	60	56	56 - 69
Olefins, vol %	20	11	13	4 - 8
Aromatics, vol %	17	29	30	23 - 36
Sulfur, wt %	<1 ppm	<1 ppm	<1 ppm	0.014 - 0.417
Nitrogen, wt %	<1 ppm	<1 ppm	<1 ppm	0.05 - 0.49

carbonyls in the methanol feed would be trapped by the gasoline synthesis unit's zeolyte catalyst and thus would not be present in the gasoline product.

TABLE 3-20. DISTRIBUTION OF OXYGENATED BY-PRODUCTS FROM FLUID-BED FISCHER-TROPSCH SYNTHESIS (63)*

Component	Wt %
Acetaldehyde	3.0
Propionaldehyde	1.0
Acetone	10.6
Methanol	1.4
Butyraldehyde	0.6
Ethanol	55.6
MEK	3.0
i-Propanol	3.0
n-Propanol	12.8
2-Butanol	0.8
Dimethyl Ketone-Methylpropyl Ketone	0.8
i-Butanol	4.2
n-Butanol	4.2
n-Butylketone	0.2
2-Pentanol	0.1
n-Pentanol	1.2
C_6 + alcohols	0.6

*The sum of reported component weight percentages does not equal 100%.

TABLE 3-21. METHANOL CONVERSION UNIT FEED AND PRODUCT COMPOSITION (1)
(Basis: 100 kmol Methanol in Feed)

Component Names	Feed	Product
Coke (as $CH_{0.8}$)	.000	.128
Acetone	.000	.129
Formic Acid	.000	.163
Methanol	100.000	.000
Dimethylether	.000	.000
Water	7.529	106.951
Carbon Monoxide	.000	.017
Carbon Dioxide	.000	.053
Hydrogen	.000	.040
Methane	.000	.746
Ethane	.000	.193
Ethene	.000	.018
Propene	.000	1.474
Propane	.000	.064
n-Butane	.000	.665
i-Butane	.000	2.155
Butenes	.000	.270
n-Pentane	.000	.268
i-Pentanes	.000	2.353
Pentenes	.000	.435
Cyclopentane	.000	.047
Methylcyclopentane	.000	.214
n-Hexane	.000	.113
i-Hexanes	.000	1.991
Hexenes	.000	.297
Methylcyclohexane	.000	.062
n-Heptane	.000	.026
i-Heptanes	.000	.786
Heptenes	.000	.292

(Continued)

TABLE 3-21. (Continued)

Component Names	Feed	Product
1,3-Dicyclopentane, cis	.000	.233
i-Octanes	.000	.228
Octenes	.000	.301
n-Propylcyclopentane	.000	.299
n-Nonane	.000	.015
i-Nonanes	.000	.084
Nonenes	.000	.116
n-Butylcyclopentane	.000	.071
i-Decanes	.000	.024
Decenes	.000	.045
Benzene	.000	.036
Toluene	.000	.280
Ethylbenzene	.000	.070
m- + p-Xylenes	.000	.876
o-Xylene	.000	.240
1,2,4-Trimethylbenzene	.000	.818
1,3,5-Trimethylbenzene	.000	.034
p-Ethyltoluene	.000	.292
i-Propylbenzene	.000	.014
1,2,4,5-Tetramethylbenzene	.000	.436
1,2,3,5-Tetramethylbenzene	.000	.063
1,2,3,4-Tetramethylbenzene	.000	.023
p-Diethylbenzene	.000	.198
Penta-Methylbenzene	.000	.068
2-Methylnaphthalene	.000	.017
Total kmol	107.529	124.832
Weight (kg)	3,339.846	3,339.846

3.5.4 Substitute Natural Gas (SNG)

The primary constituent of the SNG product (Stream 107) is methane with smaller quantities of H_2, CO, CO_2, N_2, and Ar. Standards for pipeline gas generally require that the CO content be less than 1000 ppmv, and it is expected that the crude SNG product would be sufficiently upgraded to meet this criterion. Trace quantities of metal carbonyls may be produced during catalytic methanation, during gasification, or by reaction of CO and Ni or Fe in piping. Nickel carbonyl at concentrations of about 0.01 ppmv was found in product gas from the Lurgi gasifier at Westfield, Scotland (60). Operators of the Lurgi gasifier at Sasol, South Africa, reported that carbonyls were not present in measurable concentrations in the product gas from their facility (69). Recent data from the Kosovo, Yugoslavia, Lurgi facility indicate that carbonyls are not present to any appreciable extent in the desulfurized process gases leaving the Rectisol unit (70). Carbonyl formation trends are expected to be similar for K-T and Lurgi gasification systems.

3.5.5 LP Gas

The LP gas (Stream 106) from F-T synthesis will consist primarily of propane and butane with smaller quantities of ethane, methane, and short-chain olefins. As discussed in Section 3.4.5, it is not expected that coal-derived LP gas will be significantly different in chemical composition than petroleum-derived LP gas. However, this has not been verified with product composition data from a commercial-scale production facility.

3.5.6 By-Product Sulfur (Stream 112)

Elemental sulfur is recovered as a by-product in the treatment of concentrated acid gases for air pollution control. The recovered sulfur may be contaminated with a number of impurities. When the Stretford process is employed, the by-product sulfur contains traces of vanadium, thiosulfate, and thiocyanate. Claus sulfur may contain carbonaceous materials to the extent that the by-product is at times termed "black sulfur." Depending on site-specific factors, the sulfur may be saleable or may need to be disposed as a waste.

3.6 AUXILIARIES

A number of non-pollution control auxiliary operations are associated with a self-sufficient K-T indirect liquefaction facility. Included in these are raw water treatment, power generation, process cooling, oxygen production, and product/by-product storage. These support operations are sources of additional waste streams which in many cases would be combined and treated with the wastes generated in the main process train. The sections below provide brief descriptions of the most important auxiliaries and define the expected characreristics of the major waste streams.

3.6.1 Raw Water Treatment

The source and characteristics of the raw water assumed for the K-T indirect liquefaction plant location are presented in Table 3-22. The component concentrations presented represent average annual conditions. Variations in raw water characteristics, while important in the design of a facility, are not addressed here because they do not greatly affect the characteristics of the plant's most environmentally significant waste streams.

Makeup water quantity and composition that determine the raw water treatment load for a K-T based indirect liquefaction facility depend primarily upon the plant location, feed coal composition, synthesis route, and the extent of condensate/wastewater reuse achievable. An accurate estimate of the makeup water requirements would require detailed site specific water and energy balances around the plant which are beyond the scope of this manual. However, rough approximations of the makeup water requirements have been made based upon the major water/steam consuming operations within the facility. These operations are process cooling, coal gasification and slag quench, raw gas cooling and dust removal, cyanide wash (water wash case), and shift conversion.

Water/steam consumption for each of these operations has been incorporated into their respective material flow estimates presented throughout this section and are summarized in Table 2-23. The largest single consumer of makeup water is the cooling water system (Section 3.6.3). Makeup requirements to the cooling system are based upon published overall thermal efficiency data for an Illinois No. 6 coal and different synthesis routes. Makeup water requirements to the gas cooling and dust removal operation (Section 3.3.1) are primarily dependent upon the soluble components in raw gas and dust, particularly chlorides, and to coal moisture which is related to coal rank. This requirement could decrease by as much as a factor of about three depending upon the feed coal composition. The other tabulated makeup water requirements are also dependent upon feed coal characteristics, but to a lesser extent, and are expected to have relatively little effect upon the total makeup water requirements.

TABLE 3-22. COMPOSITION OF RAW MAKEUP WATER

Constituent	Assumed Source of Raw Water Ohio River @ Grand Chain, Ill. (Ref. 71)
	Concentration (mg/L)
HCO_3^-	110
$SO_4^=$	60
Ca^{++}	36
Mg^{++}	9
Na^+	30
Cl^{-*}	15
TDS	250
SiO_2	6.5
pH	8.1

*Estimated from TDS minus major constituents and equivalence of cations and anions

TABLE 3-23. ESTIMATED MAKEUP WATER QUANTITY FOR A K-T BASED INDIRECT LIQUEFACTION PLANT (ILLINOIS NO. 6 COAL)

Process	Makeup Water Quantity, m^3/hr
Cooling Water	820 - 1207
Cyanide Wash	0 - 240
Gas Cooling and Dust Removal	230
Shift Conversion	160
Gasification	40
Boiler Bottom Ash Removal	13 - 80
Flue Gas Desulfurization (Power Generation)	10 - 60
TOTAL	1270 - 2020

Raw water makeup requirements can be reduced by the selective reuse of wastewaters. Systems with high makeup flow requirements, such as the cooling water, cyanide wash, and gas cooling and dust removal systems, offer the greatest potential for cost effective wastewater recycle/reuse. These systems have lower makeup quality requirements and will allow recycle of some wastewaters without extensive pretreatment. The same is true of the ash sluicing and flue gas desulfurization systems. The high quality makeup requirements to boilers make it difficult to recycle all but the highest quality wastewaters (e.g., methanation/compression condensates, boiler blowdown, and selected reclaimed wastewaters) to the boiler feedwater treatment system.

Figure 3-14 shows a raw water treatment scheme for producing makeup water in the base plant. Systems with lower quality requirements may choose to withdraw water after any step in the treatment process that meets their requirements. For example, cooling tower makeup could be supplied directly from the sedimentation/equalization ponds in cases where raw water is low in

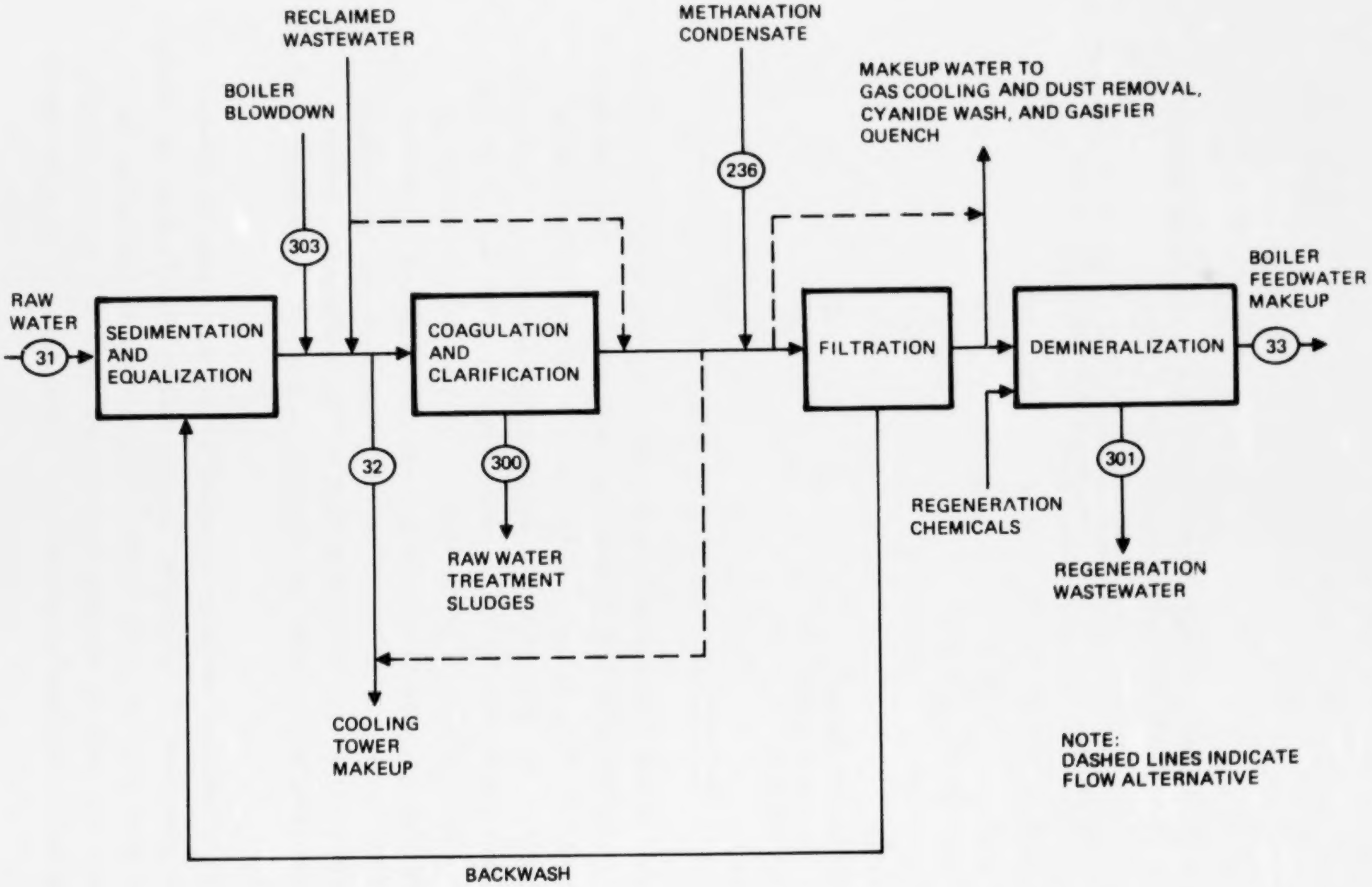
RECLAIMED WASTEWATER
BOILER BLOWDOWN
METHANATION CONDENSATE
MAKEUP WATER TO GAS COOLING AND DUST REMOVAL, CYANIDE WASH, AND GASIFIER QUENCH
236
303
BOILER FEEDWATER MAKEUP
RAW WATER
31
SEDIMENTATION AND EQUALIZATION
COAGULATION AND CLARIFICATION
FILTRATION
DEMINERALIZATION
33
32
300
301
REGENERATION CHEMICALS
RAW WATER TREATMENT SLUDGES
REGENERATION WASTEWATER
COOLING TOWER MAKEUP
NOTE: DASHED LINES INDICATE FLOW ALTERNATIVE
BACKWASH

Figure 3-14. Flow diagram for base plant raw water treatment system

hardness, alkalinity, and suspended solids. Where any of these constituents are present at high concentrations, raw water may require further treatment by softening, coagulation, clarification, or filtration prior to its use in the cooling water system.

The sedimentation and equalization step in Figure 3-14 includes withdrawal of water and storage in a reservoir. This storage provides a reliable supply of water to the facility that is independent of river flow, reduces the impact of daily water quality variations, and allows sedimentation of silts and other suspended material.

The raw water leaving the reservoir is treated in a sludge contact clarifier followed by a filter and a demineralizer. The clarifier is fed with lime, a coagulant, and a polymer to coagulate and/or flocculate fine suspended solids. The treated water then passes through a sludge bed of previously formed floc. This sludge contact enhances the agglomeration and settling characteristics of flocculated particles. An added benefit of this unit is a partial reduction in the calcium alkalinity. Boiler blowdown is recycled to the raw water treatment loop at this point to provide a mechanism for the removal of residual boiler feedwater treatment chemicals prior to demineralization. A filter is also provided to protect the demineralizers from solids carryover from the clarifier.

Demineralization is accomplished in two steps. Strong acid and base ion exchange units are used as the primary treatment step, and a mixed bed polisher is used as the secondary step. The waste streams generated as a result of this treatment scheme are discussed below.

Raw Water Treatment (Clarifier) Sludges (Stream 300)

Excess sludge consisting of calcium carbonate, magnesium hydroxide, and coagulated particulate matter is removed from the clarifier. Table 3-24 presents expected sludge production rates for varying suspended solids concentrations and estimated characteristics of this waste. The impact of suspended solids on the volume of sludge produced can be significant relative to that of the chemical precipitates. However, even with high input TSS levels, these sludges are low volume wastes which can easily be disposed of independently or with gasifier or boiler ash or with flue gas desulfurization sludges. This sludge could also be used as a neutralizing/scrubbing agent to supply a portion of the scrubber makeup alkalinity requirements for a throwaway FGD process.

TABLE 3-24. RAW WATER TREATMENT SLUDGE (STREAM 300) PRODUCTION RATES AND CHARACTERISTICS

Suspended Solids Concentrations (mg/L)	Sludge Production Rate (Mg/hr)*
0†	0.135 - 0.176
10	0.172 - 0.224
50	0.332 - 0.432
Sludge Constituents	**Sludge Compositions (wt %)‡**
$CaCO_3$	38.0
$Mg(OH)_2$	2.0
H_2O	60.0

*Sludge is assumed to be 40% solids by weight

†Clarifier sludge flows for the 0 mg/L suspended solids case derived from calculations presented in Water and Waste Treatment Data, Permutit Company, Inc., 1961

‡Sludge composition figures are for case involving 0 mg/L of suspended solids

Demineralizer Regeneration Wastewaters (Stream 301)

Table 3-25 summarizes the estimated characteristics of demineralizer regeneration wastes from the strong acid and strong base exchangers. The regeneration wastes from the mixed bed polisher will be comparable in dissolved solids to the compositions shown, but their flow will be intermittent and small compared to those from the primary ion exchange step. Regeneration wastewater flow rates (Stream 301) are calculated as 9% of the total water flow rate into the demineralizer. The boiler feedwater (Stream 33) makeup is assumed to be approximately 180 m^3/hr. At this makeup rate, the demineralizer regeneration wastewater flow rate for Illinois No. 6 coal is approximately 18 m^3/hr. Wastewater flow rates will vary by coal type and synthesis process in the same manner as the raw water makeup requirements for the boiler feedwater system. In addition, in an actual plant the regeneration wastewaters may be produced on an intermittent basis and require flow equalization prior to treatment.

TABLE 3-25. DEMINERALIZER REGENERATION WASTEWATER COMPOSITION* (STREAM 301)

Constituent	Regenerated Wastewater for Illinois No. 6 Coal Case
HCO_3^-	0
$SO_4^=$	5,037
Ca^{++}	156
Mg^{++}	89
Na^+	1,758
Cl^-	167
TDS[†]	7,207
SiO_2	72
pH	1.7

[*] All units are mg/L except pH. 33% regeneration efficiency and the use of H_2SO_4 and NaOH as regeneration chemicals assumed.

[†] Total dissolved solids calculated as a sum of the ions except SiO_2.

3.6.2 Power Generation and Process Heating

Self-sufficient indirect liquefaction facilities would require boilers for power generation and heaters for various process units including coal drying and pulverizing. In addition to boilers and heaters, other auxiliaries could include dedicated gasifiers for producing low heating value fuel gas, electrical generating units, and gas turbines. The size of the boiler would be determined primarily by the extent to which electric drivers are used versus steam or gas turbine drivers. Where electrical drivers are used, steam demand for electricity production may differ (qualitatively and quantitatively) from the case where steam drivers are used. When gas turbine drivers are used, steam requirements would be greatly reduced. A large number of possible auxiliary configurations exist, and it is beyond the scope of this manual to perform the detailed engineering required to assess all of these configurations. For purposes of analysis, electric drivers were assumed to be employed to the maximum practical extent, and the electrical energy needed is generated on-site.

A pulverized coal-fired boiler is assumed to supply the facility with all steam not produced in process waste heat boilers (e.g., gasifier, shift, synthesis). The boiler and associated systems are of conventional design using a regenerative air heater which preheats the combustion air to 533K by exchange with flue gas and an economizer to preheat boiler feedwater to 588K. Flue gas exits the system at 450K and bottom ash at 811K. Boiler thermal efficiency is approximately 90% (LHV) for Illinois No. 6 coal. Steam is used for process purposes (gasification, shift) for direct heating, in turbine drivers for motive power (e.g., compressors), and for generation of electric power. For certain purposes, steam superheating may be necessary.

As indicated earlier, 278,400 kg/hr of Illinois No. 6 coal (dry basis) is being gasified to produce approximately 113 TJ/day of fuel grade methanol and other products (methanol synthesis case). An overall plant thermal efficiency of 52.4% has been assumed for a K-T indirect liquefaction plant employing methanol synthesis (3). The amount of boiler coal needed for self-sufficient facility operation is then approximately 22,650 kg/hr (dry basis) for a K-T based methanol plant. The quantity of coal feed to the boiler will vary depending upon the type of coal being fired and the overall plant efficiency. The overall plant efficiency is different for different synthesis processes. Both Mobil M and Fischer-Tropsch syntheses are assumed to be less efficient than methanol synthesis, approximately 44.8 and 40.0%, respectively.

Coal requirements for hot gas generation associated with coal drying and pulverizing operations are included implicitly in the overall plant thermal efficiency. Therefore, using the overall thermal efficiency in estimating the coal feed to the boiler, coal which may actually be consumed in the coal preparation unit necessarily reports as boiler feed coal. The amount of coal which would be combusted in conjunction with the coal preparation operations (assuming coal is burned rather than fuel gas) is dependent upon a variety of factors including the ROM coal moisture and the residual coal moisture requirements for coal gasification. For the subject Illinois No. 6 coal, the coal consumption in coal preparation is estimated to be about 2500 kg/hr (as received basis) which corresponds to about 10% of the feed rate to the boiler in a K-T based methanol plant. Because coal combustion related to coal preparation is not unique, no attempt has been made to differentiate between flue gases associated with coal preparation and those associated with steam and power generation.

Mass flow calculations for a pulverized coal fired boiler associated with a K-T based methanol plant utilizing Illinois No. 6 coal are presented in Table 3-26.

TABLE 3-26. BOILER MASS FLOW FOR ILLINOIS NO. 6 COAL* - METHANOL SYNTHESIS CASE

Components	Molecular or Atomic Weight	Fuel Feed Stream 30			Air Feed			Flue Gas Discharge Stream 302			Bottom Ash Stream 304	
		Weight %	kg/hr	kmol/hr	mole %	kg/hr	kmol/hr	mole %	kg/hr	kmol/hr	kg/hr	kmol/hr
Gaseous												
N_2	28.01				76.47	213989.96	7639.77	73.67	214273.7	7649.9		
H_2O	18.015				2.069	3723.7	206.7	7.89	14760.2	819.33		
CO_2	44.0098				0.032	140.7	3.197	14.05	64221.7	1459.26		
O_2	31.9988				20.513	65567.5	2049.06	3.26	10821.4	338.18		
SO_2	64.0588							0.21	1406.2	21.951		
NO_2	46.0055							0.036	173.603	3.773		
CH_4 (and other hydrocarbons)	16.0426							23ppmv	3.785	0.236		
CO	28.0104							43ppmv	12.616	0.45		
CH_3CHO (and other aldehydes)	44.0530							0.14ppmv	0.063	0.00143		
Ar	39.948				0.915	3651.8	91.414	0.88	3651.8	91.414		
Total	--				100	287073.7	9990.1	100	309325	10384.5		
Solid												
C	12.011	70.757	17854.1	1486.48					321.37	26.76	35.71	2.97
H (non water)	1.0079	4.786	1207.65	1198.18								
O (non water)	15.9994	8.933	2254.1	140.89								
S	32.06	3.099	781.97	24.39					62.56	1.95	15.63	0.49
N	14.0067	1.334	336.61	24.032								
Ash	--	10.091	2546.26	--					2037.01	--	509.25	--
Water	18.0152	1.00	252.33	14.01								
Total	--	100	25233	2887.98					2420.94	28.71	560.59	3.46

*Boiler mass flows will increase by 215% for the Fischer-Tropsch synthesis case and decrease by 48% for the Mobil M synthesis case. Tabulated material flows represent engineering estimates.

An integrated facility would also have a number of small gas-fired heaters serving various process units (e.g., startup heaters). Such heaters would likely utilize sulfur-free waste gases from synthesis/fractionation operations as the most convenient fuel. Since the contribution of small heaters to sulfur and particulate emissions is expected to be minimal, pollution control alternatives (other than for NO_x) for these small heaters are not discussed in this report.

Boiler Flue Gases (Stream 302)

Table 3-26 also contains the estimated composition of the combustion flue gases for the Illinois No. 6 coal case. In addition to the high loadings of SO_2 and total particulates, these flue gases contain both particulate and volatile trace elements derived from the coal. NO_x emissions (as NO_2) were assumed to be controlled by boiler design and were estimated to be 260 ng/J. New pulverized coal fired boiler designs include some type of NO_x controls. However, if boiler design does not incorporate NO_x controls, uncontrolled NO_x emissions are expected to range from 280 ng/J to 430 ng/J. In the case of the boiler in Table 3-26, this would result in an increase of 8 to 65% in NO_x emissions. In an integrated facility, the flue gas would represent one of the major uncontrolled gaseous waste streams in terms of pollutant loading and volume. It should be noted, however, that combustion emissions are not unique to indirect liquefaction facilities and generally present no new problems for emissions control over those encountered in electric utility or industrial applications.

Boiler Bottom Ash (Stream 304) and Fly Ash (contained in Stream 302)

Although data on the characteristics of bottom and fly ash for Illinois coals are available, no data were available for the subject Illinois No. 6 coal but its bulk composition is expected to reflect the major inorganic elements found in the raw coal (see Table 3-2). Table 3-27 summarizes available data on the maximum levels of various constituents which have been reported in ash slurry waters from coal-fired boilers.

TABLE 3-27. COMPARISON OF ASH AND ASH SLURRY MAXIMUM CONCENTRATIONS (72)

	Fly Ash ppm	Bottom Ash ppm	Slurry mg/L
As	1,700	40	0.12
Ba	13,900	4,000	3.0
Cd	250	250	0.052
Cr	7,400	270	0.17
Pb	1,600	35	0.2
Hg	22	4	0.026
$NO_3^=$	--	--	--
Se	500	7.7	0.05
Ag	50	25	0.02
F^-	624	100	16.2
Cl^-	25,000	1,800	2,415
Cu	3,020	720	0.45
Fe	289,000	204,000	11.0
Mn	4,400	720	1.1
$SO_4^=$	--	--	2,300
Zn	13,000	950	2.7

Boiler Blowdown (Stream 303)

The quality of the boiler blowdown wastewater stream will be dictated by the boiler drum operating pressure. In this analysis a boiler drum operating pressure of 10.3 MPa is assumed for all synthesis process cases. Maximum silica concentrations and specific conductivity concentrations allowed in boilers at this pressure are 2.0 mg/L and 150 micromhos/cm, respectively. As the pressure of the blowdown stream is reduced to atmospheric pressure, 62% of the blowdown will flash to steam leaving a stream with a specific conductivity of approximately 400 micromhos/cm. Assuming a one to one ratio between specific conductance and total dissolved solids, this results in a maximum dissolved solids concentration of 400 mg/L. The dissolved solids will contain varying quantities of phosphates or other treatment chemicals, trace metals, and contaminants resulting from condenser leakage. This water can either be reused directly (e.g., as cooling tower makeup) or returned to the boiler feedwater pretreatment system as discussed in Section 3.6.1. It is assumed that 1% of the steam made is lost as blowdown from the steam drum. In the case of the K-T based methanol plant this is equivalent to 2145 kg/hr.

An energy efficient indirect liquefaction plant will produce large quantities of low pressure steam from process waste heat boilers. The specific conductivity of the blowdown from these low pressure boilers can range as high as 2000-5000 micromhos/cm for boilers in the 4.1 MPa to 6.9 MPa range. After flashing to atmospheric pressure, the blowdown concentrations can be two to three times higher. The design, economic, and site-specific considerations involved in determining the quantities of low pressure and high pressure steam generated in the model plants are beyond the scope of this study. Supply steam pressure, low pressure boiler makeup water treatment, and cascading reuse of high pressure boiler blowdown in the low pressure boiler system are all considerations that must be evaluated in terms of the overall water management plan at a specific site.

These blowdown flow rates can increase dramatically if severe condenser leakage occurs. However, since operation under severe leakage conditions cannot be tolerated for a long period of time, the impact of these upset conditions should be minimal.

3.6.3 Cooling Operations

In an indirect liquefaction facility, a certain portion of the input energy to the plant will be rejected as waste heat. The exact amount of heat lost will be a function of both process design and operating practices and will be highly plant-specific. Further, the cooling water evaporation rate will be a function of the amount of wet versus dry cooling used at a given site. This, in turn, will be affected by design decisions based upon climatic factors and raw water costs. Since detailed designs and heat balances were not developed for each of the indirect liquefaction facilities addressed in this manual, some simplifying assumptions were made to develop representative cooling system loads.

Table 3-28 summarizes the discharge rates expected to arise from cooling tower operations. The energy rejection rate from the cooling system was obtained by assuming an overall conversion efficiency of coal energy (HHV) to useful product energy of 52.4% in K-T indirect liquefaction plants and assuming 40% of the unrecovered thermal energy in the feed coal is rejected through evaporative cooling in a cooling tower (63). Under these assumptions, the energy rejected through the cooling tower will not be significantly affected by the different coal types employed. However, the energy rejection rate will be affected by the different overall efficiencies of the Methanol, Fischer-Tropsch, and Mobil M synthesis processes, and the variation in the energy rejection rates is directly reflected in the calculated cooling water evaporation rates for each model plant.

Discharges from cooling systems consist of: Blowdown water (Stream 307), evaporative losses (Stream 306), which include evaporated water, entrained water (drift), and stripped gases. Table 3-29 summarizes the cooling tower blowdown and drift characteristics for a cooling system operating at 5 cycles of concentration for a K-T plant using the raw waters described in Section 3.6.1 for cooling tower makeup. The blowdown/drift characteristics are intended to be typical of the concentrations expected for the Grand Chain, Illinois location where raw water is used as makeup. These characteristics do not necessarily represent optimum conditions for any given site.

TABLE 3-28. COOLING SYSTEM MAKEUP WATER REQUIREMENTS FOR A K-T INDIRECT LIQUEFACTION PLANT*

Stream Name	Stream Number	Water Rate (m^3/hr) for Illinois No. 6 Coal Case: Methanol Synthesis	Mobil M Synthesis	Fischer-Tropsch Synthesis
Cooling water evaporation rate (E)	306	660	737	966
Drift loss (D) (0.01% of circulation rate)†	306	3.7	4.1	5.4
Cooling water blowdown (BD) flow rate (five cycles of concentration)‡	307	161	180	236

[*] Assumed cooling water inlet temperature 314K, outlet temperature 303K, cooling water flow rate = 36,980 m^3/hr

[†] Calculation based on reference 74

[‡] Cycles of concentration (CC) is calculated by the following equation:
CC = (E + BD + D)/(BD + D)

In addition to the concentrations of inorganic dissolved solids shown, scale and corrosion control additives would also be present in the blowdown/drift. The control additives, especially chromate- and zinc-based inhibitors, will be a consideration in the treatment of cooling tower blowdown. Treatment for removal of these inhibitors will be discussed in Section 4.

TABLE 3-29. ESTIMATED CHARACTERISTICS OF COOLING TOWER BLOWDOWN AND DRIFT*

Blowdown/Drift Constituents	Discharge Concentration for the Illinois No. 6 Coal Case (mg/L except pH)
HCO_3^-	110
$SO_3^=$	650
Ca^{++}	180
Mg^{++}	45
Na^+	150
Cl^-	75
Total Dissolved Solids†	1210
SiO_2	33
pH	8.0

*Blowdown/drift composition estimated using raw water makeup chemistry from Section 3.6.1. Concentrations are presented for operation at 5 cycles of concentration.

†Total dissolved solids is the sum of the ions except SiO_2

The number of cycles of cooling water concentration which can be achieved in the cooling tower is largely dependent upon the total dissolved solids (particularly $CaCO_3$ and $CaSO_4$) of makeup water to the system, and a higher makeup water quality permits a larger number of cycles. Also, increasing the number of cycles of concentration has the effect of decreasing the blowdown rate for a given system. For calculation purposes, blowdown flow rates are based on cooling system operation at 5 cycles of concentration. Operation at lower cycles of concentration to allow for discharge to a surface water or operation at higher cycles in order to minimize wastewater volume and treatment equipment costs may be considered on a site-specific basis.

The cooling operation at an indirect liquefaction facility can be a critical factor in the disposal and reuse of process wastewaters. The use of treated process wastewaters as cooling tower makeup water will have a significant effect on raw water makeup requirements and discharge stream pollutant concentrations. The impact of potential emissions in both blowdown and drift resulting from the reuse of treated wastewaters will be discussed in Section 4 under air and water pollution control.

3.6.4 Oxygen Production

Oxygen required by the K-T gasification processes is assumed to be produced by standard cryogenic air separation units. Oxygen purities assumed in the gasification process mass flow calculations are based on published data for the subject coal, and no attempt has been made to force consistency. It should be noted that the purity of oxygen utilized in the gasification process affects the quantity of the purge stream from the downstream synthesis process and thereby affects synthesis efficiency. Therefore, a tradeoff exists between the energy required to produce high purity oxygen and the efficiency of the synthesis process. An analysis of optimum oxygen purities is beyond the scope of this manual.

In an air separation plant, air is compressed to 0.68 to 0.72 MPa and cryogenically cooled to facilitate distillation of oxygen, nitrogen, and noble gases (75). The oxygen stream, containing small quantities of nitrogen and argon, is compressed and sent to the gasifiers. Air and oxygen compressors can either be steam, gas, electric driven, or a combination thereof. Most of the separated nitrogen, containing small quantities of oxygen, water, and carbon dioxide, is vented to the atmosphere. However a portion of the nitrogen may be utilized as an inert gas for blanketing coal storage and transfer operations or as stripping gas for solvent regeneration in acid gas treatment. The quantity of condensate resulting from air compression depends upon atmospheric humidity and therefore is highly variable. Condensate contains only dissolved gases and can be utilized as a supplement to the plant's high quality water supply.

Oxygen requirements for the design K-T gasification system are 132,200 kg/hr for Illinois No. 6 coal, and may increase by approximately 10% for lower rank coals (23).

Production of oxygen does not directly generate environmentally significant waste streams, since chemical reactions do not take place in the air separation process nor are any chemicals added to the process streams. A gaseous waste stream containing mostly nitrogen and a liquid condensate are produced, but these streams are essentially pollutant free. Reducing the compressed air temperature prior to cryogenic cooling results in increased drift and blowdown from the cooling towers because of increased interstage compressor cooling required. Emissions indirectly associated with the compressors are dependent upon the type of power drive (either steam, gas, or electric).

3.6.5 Product and By-Product Storage

The expected production rates of upgraded liquid and gaseous fuels for the K-T indirect liquefaction plant are presented in Section 3.5. For purposes of estimating potential emissions from the storage of liquid products, a 15-day capacity is assumed in all cases. Table 3-29 provides a summary of the storage capacities, vessel types, and estimated uncontrolled mass emission rates for the various liquids. The more volatile products (e.g., LPG) are stored in pressure vessels and have no routine evaporative emissions. Methanol and gasoline are stored in floating roof tanks while diesel oil and fuel oil are stored in fixed-roof tanks.

Data on the components of evaporative emissions associated with the storage of coal derived liquid fuels are generally lacking. However, limited data are available on evaporative emissions associated with petroleum gasoline

TABLE 3-30. EVAPORATIVE EMISSION ESTIMATES FOR PRODUCT AND BYPRODUCT STORAGE*

Product	No. of Tanks	Capacity (m^3)	Tank Diameter (m)	Synthesis Case	Vapor Pressure kPa	Uncontrolled Mass Emission Rate† (kg/hr)
Methanol	1	Float Roof (3200)	18.2	Fischer-Tropsch	17.3 8.83	8,740 6,630
Methanol	2	Float Roof (45,000)	62.5	Methanol	17.3 8.83	59,790 45,360
Methanol	2	Float Roof (46,500)	64.0	Mobil M	17.3 8.83	61,250 46,470
Gasoline	1	Float Roof (22,000)	43.6	Fischer-Tropsch	49.78 33.85	21,790 20,430
Gasoline	1	Float Roof (39,000)	53.3	Mobil M	49.78 33.85	28,950 27,140
Diesel Oil	1	Fixed Roof (3600)	19.5	Fischer-Tropsch	0.080 0.046	800 500
Fuel Oil	1	Fixed Roof (940)	11.6	Fischer-Tropsch	0.00059 0.00026	9 5

*Calculations based on information contained in AP-42 (76)

†The higher values represent the month with maximum average emissions (July). The lower number represents the average annual values.

storage as indicated in Table 3-31. In addition to the paraffins and olefins listed in the table, aromatics are expected to be present in evaporative emissions in the 1 to 1000 ppm range. Since the compositions of F-T and Mobil M-gasolines are not dramatically different from those of petroleum gasolines, the gross characteristics of evaporative emissions are expected to be similar.

Product sulfur storage may result in H_2S emissions due to the evolution of dissolved sulfide. H_2S may be liberated from the liquid sulfur either inadvertantly during storage/handling operations or as a result of intentional liquid sulfur degassing to produce a sulfide-free product. Intentional degassing may be employed to minimize the fire and toxicity hazards potentially associated with liquid sulfur handling. Data are not publicly available relating to the magnitude of such potential H_2S emissions or to typical control practices in the sulfur industry. In any case, such emissions are not unique to coal gasification and hence are not further addressed in this manual.

TABLE 3-31. COMPOSITION OF EVAPORATIVE EMISSIONS FROM GASOLINE STORAGE (77)

Compound	Vol %*
Methane	1.13
Ethylene	0.001
Ethane	0.15
Propylene	0.03
Propane	0.82
Isobutane	3.03
Isobutylene	1.12
n-butane	3.53
cis-2-butane	0.84
Isopentane	6.18
n-pentane	2.89
Hexanes	0.44
Heptanes	0.16
Octanes	0.17

*Balance is air

3.7 FUGITIVE AND MISCELLANEOUS WASTES

In this section gaseous and liquid emissions from process equipment, emergency process discharges and washup/cleanup activities are discussed. Emission estimates for these streams are based upon petroleum refining experience.

3.7.1 Fugitive Organic Emissions (Stream 241)

There are many potential sources of gaseous fugitive emissions in an indirect coal liquefaction plant. These sources include: pumps, compressors, in-line process valves, pressure relief devices, open-ended valves, sampling connections, flanges, agitators, and cooling towers. Extensive tests and measurements for fugitives have been performed at petroleum refineries (78). As a result of this testing, average emission factors have been developed for fugitive emission sources such as pump seals, compressor seals, valves, etc. (79). These factors can be applied to synfuel plants because plant operations following synthesis are quite similar to those in petroleum refining. Although the plant boundary as stated in Section 3.4.5 excludes upgrading processes, these processes were included in estimating fugitive organic emissions since these processes are the major contributors to fugitive organic emissions in a K-T based indirect liquefaction facility.

Fugitive emissions estimates were made by estimating the number of each type of emission source and applying the appropriate emission factor with no adjustment for size, pressure, or flow rate. The number of pumps, compressors, and process units for synfuel plants was estimated by correlating equipment lists to the proper size synfuel plant or adjusting the equipment counts reported in conceptual designs. Equipment spares were counted in determining the number of pumps and compressors, because it was assumed that spares usually contain fluid under pressure.

The process streams associated with each piece of equipment were classified with respect to percent hydrocarbon content and hydrocarbon type.

Different factors were used for liquid streams containing light and heavy hydrocarbons. Liquid streams containing C_2 through C_9 hydrocarbons, naphtha, and other aromatic hydrocarbons were classified as light. Kerosene, diesel oil, and other heavy hydrocarbons were classified as heavy. All emission factors shown assume 100% hydrocarbon content, so all emission factors except those for compressors were multiplied by the actual hydrocarbon content for each process stream. Streams containing less than 10% hydrocarbons were neglected and those containing greater than 80% were considered to contain 100%. Gaseous streams were classified as either hydrocarbon or hydrogen depending on which was present in a greater percentage. The compressor seal emission factors for these two classifications were used as reported and not adjusted for percent hydrocarbon content.

Results of these fugitive emission calculations for K-T based indirect liquefaction facilities are given in Table 3-32. The data indicate that methanol plants are expected to have considerably lower fugitive organic emissions than Fischer-Tropsch plants. In-line valves are the single biggest contributor to total fugitive organic emissions for all facilities.

3.7.2 Non-Process/Intermittent Wastewater Streams

Fugitive process fluid leaks from sources such as pump seals, valves, and flanges will generate a "composite" waste stream with a highly variable flow and composition. In addition, drainage resulting from emergency process fluid discharges or process area washdown/cleanup activities will contribute additional intermittent aqueous wastes. All of these wastes would normally be collected in a process or oily waste sewer and routed to a common treatment system. The estimated flow rates of the combined wastewaters from these types of sources in the subject plants are summarized in Table 3-33.

These process drainage calculations are based upon refinery experience and are estimated as 2% of the total raw water makeup to the plant (80). Since the process drainage flow rate is based on the total plant raw water

TABLE 3-32. ESTIMATED TOTAL FUGITIVE ORGANIC EMISSIONS

	Uncontrolled Emission Factor (kg/hr)	Uncontrolled Emission Rates (kg/hr)		
		Fischer-Tropsch	Methanol	Mobil M
Pump Seals*				
Light Liquid Service	0.154	16.74	3.17	7.09
Heavy Liquid Service	0.029	0.52	0.23	0.38
In-Line Valves				
Gas Service	0.027	34.72	7.78	15.39
Light Liquid Service	0.011	37.02	7.09	15.68
Heavy Liquid Service	0.00023	0.14	0.06	0.09
Safety Relief Valves				
Vapor Service	0.086	24.77	5.16	11.35
Compressor Seals*				
Hydrocarbon	1.28	12.8	2.88	1.54
Hydrogen	0.10	1.8	--	--
Flanges	0.00025	1.09	1.18	2.42
Drains	0.07	10.94	2.45	4.90
Totals		140.5	30.0	58.8

*Uncontrolled emission factors for pumps and compressors represent emissions from each pump and compressor and not from each pump seal and compressor seal.

makeup rate, it will vary with coal type and synthesis process as discussed in Section 3.6.1.

TABLE 3-33. DRAINAGE ESTIMATE FROM NON-PROCESS/INTERMITTENT STREAMS

Stream	Drainage Flow Rate m^3/hr
Process drain effluent (Stream 315)*	32 - 42
Storm drain effluent (Stream 314)	47

*Flow rate based on 2% of total raw water makeup to the plant

Both the flow rate and composition of these wastewaters will vary widely among the different plants. Of course, good housekeeping and maintenance practice will minimize these flows. These wastewaters will contain oil and grease, dissolved organics, dissolved inorganics, and particulate matter in widely varying concentrations. Because the characteristics of these wastewaters will be site-specific and highly variable with time, no composition estimates were developed for these streams. The treatment of these streams and their impact on facility costs and energy usage will be discussed in Section 4.

Storm runoff water flow rates will be a function of the surface drainage area of the plant site and the annual rainfall. For calculation purposes, a plant site drainage area of 100 surface acres was used with an annual rainfall rate of 1 m/yr (81). The average storm runoff flow was estimated to be 47 m^3/hr (refer to Table 3-33).

The composition of storm runoff from the area will vary with the frequency of a rainfall occurrence and with time during a rainfall occurrence. The major contaminants potentially requiring control are total suspended solids, oil, and grease. Because of the variable, site-specific nature of the composition of this stream, no attempt has been made to develop a detailed composition.

3.7.3 Equipment Cleaning Wastes (Streams 242 and 305)

The two primary sources of equipment cleaning wastes at an indirect liquefaction facility are process equipment (Stream 242) and boiler cleaning wastes (Stream 305). Process equipment cleaning wastes will result from periodic cleanup or maintenance of equipment such as heat exchangers, pumps, and pressure vessels. The volume of cleaning waste generated will be determined by the vessel volumes, frequency of cleanup, cleaning agent used, and rinsing requirements. Cleaning waste discharges are intermittent, short duration, high flow rate occurrences.

Boiler cleaning wastes will be generated on a one to four year cycle depending on plant maintenance practices. The large volume of the boiler can result in cleaning waste dumps in excess of 3800 m^3 over short periods of time. Boiler cleaning wastes will probably be the largest single source of cleaning wastes at an indirect liquefaction facility.

The composition of equipment cleaning wastes will vary with the cleaning agent used and the material being removed. Cleaning of process equipment generally includes the removal of oils, sludges, and waxy materials using alkaline solvents. Boiler cleaning is undertaken to remove inorganic (scaling) materials and metal corrosion products with acidic and alkaline cleaning agents. Rinse volumes from both process and boiler cleaning wastes contain lower contaminant concentrations than the cleaning wastes themselves but can amount to 2 to 5 times the volume of the cleaning waste. Treatment of these wastes is difficult because of their complex composition. Despite the intermittent and large volumes of waste generated, when considered on an annual average basis, cleaning wastes are produced at relatively low flow rates compared with other wastewaters generated in an indirect liquefaction facility.

3.8 WASTE/CONTROL TECHNOLOGY INDEX

The preceding parts of this section have provided a general description of K-T based synfuels facilities and test data and engineering estimates characterizing the uncontrolled or primary waste streams expected. Section 4 of this manual presents information on the available control techniques for these primary waste streams and illustrative examples of both individual control technologies and integrated systems of control technologies applied to specific streams. As will be discussed in Section 4, residuals or secondary waste streams are generated as a result of the application of some control technologies; control of secondary waste streams is discussed in conjunction with the illustrative examples. A summary of the process streams and primary and secondary waste streams discussed in this manual is presented in Table 3-34.

To aid users in finding characterization data and control technology information for any waste stream addressed in this manual, a cross reference index was developed. This index is presented in Table 3-35 and indicates where characterization data can be found in Section 3 and where control technology information can be found in Section 4 for each primary waste stream. The waste streams in Table 3-35 are grouped by the operation or auxiliary process from which they originate and then further grouped within each operation by waste medium. Similar types of information on secondary waste streams are presented in Table 3-36. The entries in Table 3-36 are not meant to imply that those streams will necessarily be found in K-T based facilities, but that if the control techniques listed are used, then those streams will be produced.

TABLE 3-34. STREAM INDEX

Main Process Streams (Numbers 1-99)

Coal Preparation

1. Run of mine coal
2. Prepared coal to gasifier

Gasification

3. Gasifier steam
4. Oxygen
5. Quench ring water to gasifier
6. Raw quenched gas from waste heat boiler

Gas Purification and Upgrading

7. Raw gas from washer cooler
8. Raw gas after NO_x reduction
9. Raw compressed gas
10. Compressed gas after cyanide wash
11. Desulfurized gas to shift conversion
12. Desulfurized shift conversion bypass gas
13. Shift gas to CO_2 absorber
14. Synthesis gas
15. Nitrogen strip gas

Product Synthesis

20. Crude methanol
21. Crude Mobil M-gasoline products
22. Crude Fischer-Tropsch synthesis products
23. Methanation product gas
24. CO_2-free SNG
25. Purge gas to methanation

(Continued)

TABLE 3-34. (Continued)

Auxiliaries

30. Prepared coal to boiler
31. Plant raw water
32. Cooling tower makeup water
33. Boiler feed water

Product and By-Product Streams (Numbers 100-199)

Fischer-Tropsch Synthesis

100. Gasoline
101. Diesel oil
102. Heavy oil
103. Methanol
104. Ketones
105. Heavy alcohols
106. LPG
107. SNG

Methanol Synthesis

108. Fuel grade methanol

Mobil M-gasoline Synthesis

109. Gasoline
110. Mixed butanes
111. Propane

By-Products

112. Sulfur

Discharge Streams from the Main Process Train (Numbers 200-299)

Coal Preparation

200. Fugitive dust from raw coal storage

(Continued)

Coal Preparation (continued)

201. Raw coal storage runoff
202. Fugitive dust from coal screening and crushing
203. Fugitive dust from screened/crushed coal transfer
204. Fugitive dust from coal pulverizing
205. Fugitive dust from pulverized coal storage and feeding
206. Emissions from thermal dryers

Gasification

207. Quenched slag
208. Transient waste gases

Gas Purification and Upgrading

209. Dewatered dust
210. Cooling and dust removal blowdown
211. Raw gas compression and cooling condensate
212. Spent NO_x reduction catalyst
213. Aqueous still bottoms from methanol based cyanide wash
214. Sour flash gas from cyanide wash
215. Cyanide wash water
216. H_2S-rich offgas
217. Spent shift catalyst
218. Shift condensate blowdown
219. CO_2-rich offgas
220. Rectisol condensate/still bottoms
221. Spent sulfur guard

Product Synthesis

222. Spent F-T catalyst
223. F-T wastewater
224. Fractionator light gas
225. Methanol synthesis expansion gas

(Continued)

TABLE 3-34. (Continued)

Gas Purification and Upgrading (continued)

226. Methanol synthesis purge gas
227. Spent methanol synthesis catalyst
228. Methanol distillation offgas
229. Methanol distillation wastewater
230. Fuel gas from Mobil synthesis
231. Mobil synthesis catalyst regeneration/decommissioning offgas
232. Spent Mobil catalyst
233. Mobil synthesis condensate
234. Mobil fractionator offgas
235. CO_2 removal condensate
236. Methanation condensate
237. Methanation catalyst regeneration/decommissioning offgas
238. Spent methanation catalyst
239. CO_2 offgas from SNG purification
240. Dehydration offgas

Miscellaneous Waste Streams

241. Fugitive organic emissions
242. Equipment cleaning wastes

Discharge Streams from Auxiliary Processes (Numbers 300-399)

Raw Water Treatment

300. Raw water treatment sludges
301. Demineralizer regeneration wastewater

Power Generation

302. Flue gases from power generation
303. Boiler blowdown
304. Boiler bottom ash
305. Boiler cleaning wastes

(Continued)

TABLE 3-34. (Continued)

Cooling Tower

306. Cooling tower evaporation/drift
307. Cooling tower blowdown

Product/By-Product Storage

308. Evaporative emissions from methanol storage
309. Evaporative emissions from gasoline storage
310. Evaporative emissions from diesel oil storage
311. Evaporative emissions from heavy oil storage
312. Evaporative emissions from ketones storage
313. Evaporative emissions from heavy alcohols storage

Miscellaneous

314. Storm drain effluent
315. Plant process drains effluent

Discharge Streams from Pollution Control Processes (Numbers 400-499)

Coal Preparation

400. Coal particulates from coal preparation

Gasification

No secondary waste streams are associated with this process area.

Gas Purification and Upgrading and Product Synthesis*

401. Catalyst regeneration offgas from Claus process
402. Claus spent catalyst
403. Claus sulfur
404. Stretford oxidizer vent gas
405. Sour condensate from Beavon/Stretford process

(Continued)

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*Secondary waste stream numbers 401 to 414 result from control processes treating waste streams from gas purification and upgrading operations only. Secondary waste stream numbers 415 to 422 result from control processes treating combined waste streams from gas purification and upgrading, and product synthesis

TABLE 3-34. (Continued)

Gas Purification and Upgrading and Product Synthesis (continued)

406. Stretford solution purge
407. Beavon/Stretford spent catalyst
408. Beavon/Stretford sulfur
409. SCOT sour condensate
410. SCOT spent catalyst
411. Wellman-Lord acidic wastewater
412. Wellman-Lord thiosulfate/sulfate purge
413. Flue gas from fluidized bed boiler
414. Spent bed media from fluidized bed boiler
415. Activated sludge solid waste
416. Sulfide/cyanide offgas
417. Filtration backwash
418. Denitrification waste sludge
419. Evaporation/drift from cooling tower concentration
420. Regeneration offgas from granular activated carbon
421. Offgas from liquid waste incinerators
422. Offgas from solid waste incinerators

Auxiliaries

423. Boiler fly ash from ESPs/fabric filters
424. FGD sludge from lime/limestone scrubbing
425. Thiosulfate/sulfate purge from Wellman-Lord FGD process
426. Sulfur from Wellman-Lord FGD process

TABLE 3-35. CROSS-REFERENCE INDEX FOR PRIMARY WASTE STREAMS

Stream Identification	PCTM Section Reference	
	Waste Characterization	Control Techniques
Coal Preparation		
Gaseous Waste Streams		
Fugitive dust emissions from raw coal storage piles (Stream 200)	Section 3.1	Section 4.1.4
Crushing/screening/transfer/pulverizing dust (Streams 202, 203, 204)	Section 3.1	Section 4.1.6
Particulate emissions from prepared coal storage and feeding (Stream 205)	Section 3.1	Section 4.1.6
Emissions from thermal dryers (Stream 206)	Section 3.1	Section 4.1.2.1
Aqueous Waste Streams		
Raw coal storage pile runoff (Stream 201)	Section 3.1	Section 4.2.1
Coal Gasification		
Gaseous Waste Streams		
Transient waste gases (Stream 208)	Section 3.2	Section 3.2
Solid Waste Streams		
Quenched slag (Stream 207)	Section 3.2	Section 4.3.2.1

(Continued)

TABLE 3-35. (Continued)

Stream Identification	PCTM Section Reference	
	Waste Characterization	Control Techniques
Gas Purification and Upgrading		
Gaseous Waste Streams		
Sour flash gas from cyanide wash - water wash case (Stream 214a)	Section 3.3.4	Sections 4.1.1.2 and 4.1.1.5
Sour flash gas from cyanide wash - methanol wash case (Stream 214b)	Section 3.3.4	Sections 4.1.1.2 and 4.1.1.5
H_2S-rich offgas (Stream 216)	Section 3.3.6	Sections 4.1.1.1 and 4.1.1.5
CO_2-rich offgas (Stream 219)	Section 3.3.6	Section 4.1.1.3
Aqueous Waste Streams		
Cooling and dust removal blowdown (Stream 210)	Section 3.3.1	Section 4.2.3.3
Raw gas compression and cooling condensate (Stream 211)	Section 3.3.3	Section 4.2.3.2
Cyanide wash water (Stream 215)	Section 3.3.4	Section 4.2.3.1
Cyanide wash still bottoms - methanol wash case (Stream 213)	Section 3.3.4	Section 4.2.1
Shift condensate blowdown (Stream 218)	Section 3.3.5	Section 4.2.1
Rectisol condensate/still bottoms (Stream 220)	Section 3.3.6	Section 4.2.1

(Continued)

TABLE 3-35. (Continued)

Stream Identification	PCTM Section Reference	
	Waste Characterization	Control Techniques
Solid Waste Streams		
Dewatered dust (Stream 209)	Section 3.3.1	Section 4.3.2.2
Spent NO_x reduction catalyst (Stream 212)	Section 3.3.2	Section 4.3.5
Spent shift conversion catalyst (Stream 217)	Section 3.3.5	Section 4.3.5
Spent sulfur guard (Stream 221)	Section 3.3.7	Section 4.3.5
Product Synthesis		
Gaseous Waste Streams		
Mobil synthesis catalyst regeneration offgas (Stream 231)	Section 3.4.6	Section 4.1.3.2
Methanation catalyst decommissioning offgas (Stream 237)	Section 3.4.6	Section 4.1.3.2
CO_2 offgas from SNG purification (Stream 239)	Section 3.4.6	Section 4.1.3.1
Dehydration offgas (Stream 240)	Section 3.4.6	Not evaluated
Liquid Waste Streams		
Methanol distillation wastewater (Stream 229)	Section 3.4.6	Section 4.2.2.3
F-T wastewater (Stream 223)	Section 3.4.6	Section 4.2.2.2

(Continued)

TABLE 3-35. (Continued)

Stream Identification	PCTM Section Reference	
	Waste Characterization	Control Techniques
Mobil synthesis condensate (Stream 233)	Section 3.4.6	Section 4.2.2.1
Methanation condensate (Stream 236)	Section 3.4.6	Section 4.2.1
Solid Waste Streams		
Spent methanol synthesis catalyst (Stream 227)	Section 3.4.6	Section 4.3.5
Spent F-T catalyst (Stream 222)	Section 3.4.6	Section 4.3.5
Spent Mobil catalyst (Stream 232)	Section 3.4.6	Section 4.3.5
Spent methanation catalyst (Stream 238)	Section 3.4.6	Section 4.3.5
Auxiliaries		
Gaseous Waste Streams		
Boiler flue gases (Stream 302)	Section 3.6.2	Section 4.1.2.1
Cooling tower evaporative losses (Stream 306)	Section 3.6.3	Not evaluated
Evaporative emissions from product and by-product storage (Streams 308 through 313)	Section 3.6.5	Section 4.1.5.1
Fugitive organic emissions (Stream 241)	Section 3.7.1	Section 4.1.5.2
Aqueous Waste Streams		
Demineralizer regeneration wastewaters (Stream 301)	Section 3.6.1	Section 4.2.1

(Continued)

TABLE 3-35. (Continued)

Stream Identification	PCTM Section Reference	
	Waste Characterization	Control Techniques
Boiler blowdown (Stream 303)	Section 3.6.2	Section 4.2.1
Cooling tower blowdown (Stream 307)	Section 3.6.3	Section 4.2.1
Process drain effluent (Stream 315)	Section 3.7.2	Section 4.2.1
Storm drain effluent (Stream 314)	Section 3.7.2	Section 4.2.1
Equipment cleaning wastes (Streams 242 and 305)	Section 3.7.3	Section 4.2.1
Solid Waste Streams		
Raw water treatment sludges (Stream 300)	Section 3.6.1	Section 4.3.2.8
Boiler bottom ash (Stream 304)	Section 3.6.2	Section 4.3.2.3

TABLE 3-36. CROSS-REFERENCE INDEX FOR SECONDARY WASTE STREAMS

Control Technology/Secondary Waste	PCTM Section Reference Waste Characterization	Control Technique	Control Technology Appendix*
Air Pollution Control			
Claus Process			A-6
Catalyst regeneration offgas (Stream 401)		Not evaluated	
Spent catalyst (Stream 402)	Sections 4.1.1 and 4.1.1.1	Section 4.3.5	
Sulfur (Stream 403)		Section 4.3.3.1	
Beavon/Stretford Process			A-9
Stretford oxidizer vent gas (Stream 404)	Sections 4.1.1 and 4.1.1.1	Not evaluated	
Sour condensate (Stream 405)	Sections 4.1.1 and 4.1.1.1	Section 4.2.3.4	
Stretford solution purge (Stream 406)	Sections 4.1.1 and 4.1.1.1	Section 4.2.3.4	
Spent catalyst (Stream 407)	Sections 4.1.1 and 4.1.1.1	Section 4.3.5	
Sulfur (Stream 408)		Section 4.3.3.1	
Shell Claus Offgas Treatment (SCOT) Process			A-8
Sour condensate (Stream 409)	Section 4.1.1 and 4.1.1.1	Section 4.2.3.4	

(Continued)

TABLE 3-36. (Continued)

Control Technology/Secondary Waste	PCTM Section Reference Waste Characterization	 Control Technique	 Control Technology Appendix*
Spent catalyst (Stream 410)	Sections 4.1.1 and 4.1.1.1	Section 4.3.5	
Wellman-Lord Process			A-10
Acidic wastewater (Stream 411)	Sections 4.1.1 and 4.1.1.1	Section 4.2.3.4	
Thiosulfate/sulfate purge (Stream 412)	Sections 4.1.1 and 4.1.1.1	Section 4.2.3.4	
Electrostatic Precipitators			A-13
Boiler fly ash (Stream 423)	Section 3.6.2	Section 4.3.2.4	
Limestone Scrubbing			A-20
FGD sludge (Stream 424)	Section 4.1.2	Section 4.3.2.5	
Wellman-Lord FGD Process			A-10
Thiosulfate/sulfate purge (Stream 425)	Section 4.1.2	Section 4.2.3.4	
Sulfur (Stream 426)		Section 4.3.3.1	
Coal Particulate Dry Collectors			A-11,A-12
Coal particulate (Stream 400)	Section 3.1	Section 4.3.3.2	

(Continued)

TABLE 3-36. (Continued)

Control Technology/Secondary Waste	PCTM Section Reference Waste Characterization	 Control Technique	 Control Technology Appendix*
Water Pollution Control			
Activated Sludge			B-10,B-23
Sulfide/cyanide offgas (Stream 416)	Section 4.2.4	Section 4.1.1.4	
Waste sludge (Stream 415)	Sections 4.2.2.1, 4.2.3.1, 4.2.3.2	Section 4.3.4	
Filtration			B-4
Backwash (Stream 417)	Section 4.2.2.1	Section 4.2.2.1	
Biological Denitrification			B-23
Waste sludge (Stream 418)	Sections 4.2.3.1 and 4.2.3.2	Section 4.3.4	
Cooling Tower Concentration			B-18
Evaporation/drift (Stream 419)	Sections 4.2.2.1, 4.2.3.1, 4.2.3.2	Not evaluated	
Granular Activated Carbon			B-15
Regeneration offgas (Stream 420)	Section 4.2.2.1	Section 4.2.2.1	
Incineration			B-17
Flue gas (Stream 421)	Section 4.2.2.1	Section 4.2.2.1	

(Continued)

TABLE 3-36. (Continued)

Control Technology/Secondary Waste	PCTM Section Reference	
	Waste Characterization	Control Technique
Solid Waste Management		
Fluidized Bed Combustion Boiler		
Boiler flue gas (Stream 413)	Section 4.3.2.2	Section 4.1.2.3
Spent bed media (Stream 414)	Section 4.3.2.6	Section 4.3.2.6
Incineration		
Flue gas (Stream 422)	Section 4.3.4.1	Section 4.3.4.1

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[*] The Control Technology Appendices for the PCTMs are compiled in a separate volume.

SECTION 4

EVALUATION OF POLLUTION CONTROL TECHNOLOGY

At the present time, no K-T based indirect liquefaction plants are operating in the United States, although the K-T process is widely used in other countries for the production of hydrogen (primarily for ammonia) and fuel gas. The emphasis on pollution control which has been incorporated into designs for facilities abroad is generally less than that which is anticipated for U.S. facilities. Thus, directly applicable performance data for most pollution control technologies are quite limited. The potential applicability of most pollution control technologies to waste streams identified in Section 3 has, therefore, been inferred from their use in similar applications in industries such as petroleum refining, coke production, natural gas processing, coal cleaning, and electrical utilities. This section provides an evaluation of the control methods which may be adapted from other industries and from general pollution control practice, and definition of the principal limitations of these controls methods in K-T based synfuels plants. Control alternatives evaluated include process modifications (relative to existing designs) in addition to add-on controls.

Approach

In this section a wide variety of potentially applicable pollution control technologies are discussed. In addition, illustrative examples of the application of individual control technologies to specific waste streams as well as the application of integrated systems of control technologies to specific waste streams are presented for each waste medium (e.g., gaseous, aqueous, and solid waste).

Descriptions of the pollution control technologies presented in this section are based upon more detailed descriptions provided in the Control Technology Appendices. Performance data for control technologies have been obtained primarily from the open literature and have been supplemented by vendor-supplied data in some cases. The capabilities of various controls have not usually been assessed on a design-specific basis, but rather upon a generalized basis derived from test results and/or engineering studies of the subject technologies. Example performance levels used for evaluation purposes encompass most of the published data. Therefore, only limited data referencing is provided in Section 4; detailed references are available in the Control Technology Appendices.

In many cases, performance can only be estimated in terms of control of major constituents (e.g., hydrogen sulfide) or gross parameters (e.g., COD) since often no information is available for removal efficiencies of specific substances. Further, even in those cases where substance-specific performance information exists for a control technology, accurate or complete characterization of the waste stream requiring control may be lacking. In the final analysis, the capabilities of controls can only be accurately evaluated by testing at operating facilities or at smaller units from which data can be confidently extrapolated to commercial size. The performance estimates in this document are believed to reflect the best information publicly available based on actual experience and on engineering analysis.

In providing example applications of pollution control technologies, waste streams unique to K-T based synfuels facilities and large volume/high loading waste streams have been emphasized. The source and characteristics of these waste streams have been detailed in Section 3, and those characteristics of principal significance with regard to the application of pollution control technologies are reiterated in this section. It should be noted, however, that Section 3 does not reflect the design of a specific facility, but incorporates key features of a number of existing and proposed facilities. Some of the waste streams identified in Section 3 may not be found in all facilities. Further, in a specific facility, some streams encountered may differ significantly in size and characteristics from analogous streams discussed in this section, and controls other than those cited in the examples may be more appropriate. For these reasons the reader is encouraged to consider design-specific waste stream characterization data whenever they are available and to use the detailed Control Technology Appendices for estimating the applicability and performance of specific controls to waste streams. The control examples in this section emphasize the Illinois No. 6 coal and the the base plant defined in Section 3. Effects of coal characteristics and design modifications are discussed in those cases where either may significantly influence the control performance or cost.

Reliability of pollution control processes in U.S. coal conversion facilities will depend largely upon the time required to determine the optimum operating conditions and the emphasis placed upon operation and maintenance. In essentially any industry, the introduction of a new process or modification of an older process for application to new streams meets with unexpected problems relating to both design features and operating practices. Thus, some shakedown period must be expected where process performance, efficiency, and on-stream time will improve. Once a process is properly characterized for a specified application, reported reliability in terms of on-stream time and performance levels may still vary among facilities. Sometimes the specific design is a factor, but reliability also reflects the emphasis placed upon operation and maintenance. A properly trained operating crew and a regular maintenance regimen can significantly improve the reliability of well designed pollution control equipment.

Because most of the potentially applicable pollution control technologies have not been employed in synthetic fuels facilities, few directly related reliability data are available. Further, the overall characteristics and variability of waste streams in coal conversion facilities are often significantly different from those encountered in other industries. As a result, reliability data accumulated in other industries may not be directly applicable to coal conversion processes. Published reliability data for control technologies in other industrial applications are summarized in the Control Technology Appendices. However, in this section, reliability is discussed primarily in terms of those factors which have a major influence upon process operation and stability.

Organization

The pollution control technology evaluations are presented according to the medium to which the technologies apply. Technologies applying to gaseous, aqueous, and solid waste media are discussed in Sections 4.1, 4.2, and 4.3, respectively. Included in each of these sections are (1) a summary of waste stream characteristics which are significant with respect to the application of pollution controls (detailed characterization estimates are presented in Section 3), (2) a brief description of the performance and costs of potentially applicable pollution control technologies, (3) examples of the performance and cost of individual pollution control technologies applied to specific waste streams, and (4) examples of the performance and cost of integrated pollution control systems.

Gaseous waste streams may be categorized according to the principal pollutants which are present and, in general, different controls or groups of controls are applicable to each category. Therefore, the technology descriptions and control examples presented in Section 4.1 (Gaseous Medium) are by waste stream categories or source types to which they apply.

Source type categorizations may also be made for aqueous and solid wastes. Waste streams in these media, however, often lend themselves to treatment by control technologies which may be applicable to several individual source types or to combinations of source types. Therefore, in Sections 4.2 and 4.3 (Aqueous Medium and Solid Waste Management, respectively) potentially applicable pollution control technologies are discussed at the beginning of the section prior to the presentation of control examples.

Costing Methodology

Capital and operating cost estimates have been developed for the control processes discussed in this section. These cost estimates are based primarily on estimates contained in non-proprietary published literature. The estimates are provided to give the reader an indication of the costs of controls that are applicable to K-T based synthetic fuels plants. It was beyond the scope of this manual to develop detailed engineering designs necessary for highly accurate cost estimation.

There are three general factors that lead to uncertainties in the cost estimates provided. These are related to the assumptions used to develop material and energy balances, the level of accuracy of the published cost data used, and the general methodology used to apply the acquired cost data to the control processes addressed in this manual.

Material and energy balances were derived mainly from commercial synfuels tests, from data from analog industries, and from results of engineering calculations, as described in Section 3. The level of accuracy in specifying the flow rates and quality of input streams to controls will affect the accuracy of the resulting cost estimates.

Sources of cost data used in this manual are published costs for processes applied to similar streams in related industries, costs from published detailed design studies, and vendor quotes. The accuracy of cost data taken from published sources is influenced by the details of the design upon which the cost was based, the cost methodology, and the degree of similarity of the streams. Also, the accuracy of the estimates and the components included in the cost estimates (e.g., contingency reserves and working capital), are not always provided in the reference. Thus, extrapolation of these costs to the stream being treated in this manual will also introduce uncertainties.

The costing methodology used in this manual (see Appendix A for details) also introduces some uncertainties. Other estimators may have used different factors or weighted them differently. In addition, available cost estimates were adjusted to a 1980 basis using the Chemical Engineering plant cost annual index. It is also possible that recent advances in the state-of-the-art are not reflected in some of the resulting cost estimates.

As a result of the above influences, the accuracy of the cost information presented will vary from control to control. However, the cost information presented is believed to be adequate for the use intended.

Capital costs presented are total depreciable investment costs. Included in the total depreciable investment costs are (1) installed equipment costs, (2) indirect installation charges (including construction and engineering costs, contractor fees, and contingency), and (3) interest during construction. Total annualized costs presented include (1) labor and maintenance, (2) raw materials, utilities, chemicals, and catalysts, (3) overhead charges, and (4) capital related charges (including interest on working capital, taxes, insurance, and capital recovery). The same methodology was used to calculate capital and annualized costs for both the base plant and pollution controls. Details of that methodology and other pertinent assumptions and bases which were used to develop the cost estimates are presented in Appendix A.

4.1 GASEOUS MEDIUM

Gaseous waste streams, or uncontrolled gaseous emissions, originating from the main process train and from non-pollution control auxiliary processes in a K-T based gasification facility, were identified in Section 3. Characteristics of these streams and additional gaseous waste streams generated by pollution control processes are summarized in Table 4-1. In terms of volume and pollutant loading, the most important streams in the subject facilities are Rectisol acid gases, flash gases from cyanide washing, and combustion flue gases. Pollutants of primary concern in these streams are reduced sulfur species, SO_2, HCN, CO, and particulates. These pollutants may also be present in intermittent transient waste gases generated during startup, shutdown, and transient operations. Smaller volume waste gases such as regeneration/decommissioning offgases, CO_2-rich offgases from SNG purification, condensate depressurization offgases, fugitive organic emissions, and evaporative emissions may contain non-methane organics (or VOC-volatile organic compounds), CO, or particulate emissions. An additional source of particulate emissions is the coal preparation operation.

The waste streams in Table 4-1 may be regrouped into two broad categories, those which are unique to gasification or synthesis operations and those which are not unique. Non-unique streams are associated with auxiliary operations within an integrated facility. In Section 3, gaseous wastes were identified and characterized from the standpoint of their origin in an integrated plant. Table 4-2 is a regrouping of these waste streams according to the major types of potential pollutants which they contain. Streams unique to K-T facilities are primarily those containing reduced sulfur, non-methane organics, and smaller amounts of HCN and NH_3. These streams are: (1) Rectisol acid gases, (2) flash gases from the cyanide wash, and (3) gasifier transient waste gases. Another unique stream which contains VOC, CO, and/or particulates is the Mobil M-catalyst regeneration offgas. Non-unique streams common to

TABLE 4-1. SUMMARY OF ESTIMATED GASEOUS WASTE STREAM CHARACTERISTICS IN K-T BASED INDIRECT LIQUEFACTION FACILITIES

Stream Name	Constituent Concentration (volume percent, dry basis)									Flow Rate (kmol/hr dry basis unless otherwise specified)*
	H_2S	COS	SO_2	VOC	CO	NH_3	HCN	NO_x	Particulate	
Streams from Main Process Train										
Dust from coal preparation (streams 200, 202 to 206)	--	--	--	--	--	--	--	--	Present	100-2200 kg/hr (maximum rate) 70-1400 kg/hr (average rate)
Transient waste gases (stream 208)	<1	<0.1	<1	<0.1	<62	<0.02	<0.01	--	Present	Unknown but small on an average basis
Sour gas from cyanide wash flash - water wash case (stream 214a)	11	--	--	--	--	--	0.05	--	--	22
Sour gas from cyanide wash flash - methanol wash case (stream 214b)	44	3	--	2	26	--	15	--	--	16
H_2S-rich Rectisol offgas (stream 216)	42	5	0.02	1	--	--	0.06	--	--	535
CO_2-rich Rectisol offgas (stream 219)	0.0005	0.0008	--	Present	1	--	--	--	--	10,064
Streams from synthesis processes										
Mobil synthesis catalyst regeneration offgas (stream 231)	--	--	--	Present	1	--	--	--	Present	200 maximum; 100 average
Methanation catalyst decommissioning offgas (stream 237)	--	--	--	--	Present	--	--	--	Present	Unknown but very infrequent
CO_2-rich offgas from SNG purification (stream 239)	--	--	--	0.2	--	--	--	--	--	273
Fugitive organic emissions (stream 241)	--	--	--	Present	--	--	--	--	--	30-140 kg/hr
Streams from auxiliary processes										
Flue gases from power generation (stream 302)	--	--	0.2	0.01	0.03	--	--	0.04	10 g/m^3	5400-32711
Evaporative emissions from product storage (stream 308 to 313)	--	--	--	Present	--	--	--	--	--	2.5-7.5 kg/hr average 2.8-9.3 kg/hr max.
Streams from pollution control processes										
Fugitive emissions from waste-water treatment (stream 416)	Present	--	--	--	--	Present	Present	--	--	Unknown
Flue gas from K-T dust incineration (stream 413)	--	--	0.2	--	Present	--	--	0.02	10 g/m^3	7419

*For a plant with an input to the gasifier of 278 Mg/hr dry Illinois No. 6 coal.

TABLE 4-2. CATEGORIZATION OF GASEOUS WASTE STREAMS ACCORDING TO SOURCE TYPE IN K-T INDIRECT LIQUEFACTION FACILITIES

Source Type	Stream Name and Origin	Factors Affecting Flow Rate and Pollutant Loading
Acid gases containing reduced sulfur/nitrogen, organics and CO	Rectisol acid gases (stream 216)	Coal sulfur; coal rank; acid gas removal selectivity
	Flash gases from cyanide wash (stream 214)	Coal sulfur; cyanide wash solvent; process pressure; coal rank may influence HCN formation
Combustion gases	Boiler flue gases (stream 302)	Overall plant thermal efficiency; coal ash and sulfur; boiler design and efficiency
	Process heater flue gases	Tend to be design/synthesis specific; not related to coal parameters
	Flue gas from K-T dust incineration (stream 413)	Coal rank; coal ash and sulfur; combustor design and efficiency; dust feed rate
Organic and CO containing gases	Catalyst regeneration/decommissioning offgases (stream 237)	Tends to be design specific; not related to coal parameters
	CO_2-rich offgas from SNG purification (stream 239)	Tends to be design specific; not related to coal parameters
Fugitive dust	Dust from coal storage (stream 200)	Coal physical properties (particle size, moisture, density, etc.); site-specific climatological factors
Fugitive VOC	Product storage evaporation emissions (streams 308 to 313)	Synthesis process; product slate
	Process equipment fugitives (stream 241)	Synthesis process; upgrading steps employed; plant design
Fugitive particulate	Particulate from coal handling and preparation (streams 202 to 206)	Coal physical properties; coal preparation operations and layout

all K-T plants would include coal combustion flue gases, coal preparation dust, product storage emissions, and process VOC emissions.

In each of the subsections that follow, controls which may be applicable to the above gaseous wastes are identified. For those technologies for which data are available, the expected performance and costs are provided. Technology descriptions are provided at the beginning of each subsection as follows:

- Section 4.1.1 provides descriptions of bulk sulfur removal, tailgas treatment, and incineration technologies.
- Section 4.1.2 provides descriptions of NO_x removal, particulate removal, and SO_2 removal technologies.
- Section 4.1.3 refers to the Section 4.1.1 incineration technology description.
- Section 4.1.4 provides descriptions of technologies for suppression of fugitive dust from coal storage piles.
- Section 4.1.5 provides descriptions of fugitive VOC control technologies.
- Section 4.1.6 provides descriptions of technologies for suppression, capture, and collection of fugitive particulates from material conveying and processing.

In many cases control of gaseous pollutants involves both inherent process design features and tradeoffs among processes. Further, some waste gases are combined for treatment rather than handled separately. Accordingly, example approaches to the control of pollutants in integrated facilities are provided. Sufficient detail is included in these examples such that overall emissions reductions and costs can be seen. In the discussions below, emphasis is on the unique streams rather than on those streams for which information about control may be found in other documents.

4.1.1 Acid Gases Containing Reduced Sulfur/Nitrogen, Organics, and/or Carbon Monoxide

As discussed in Section 3, K-T based coal gasification plants will employ the Rectisol process for removal of sulfur compounds, CO_2, and HCN from the washed product gas. Regeneration of the methanol solvent produces waste gases enriched with these acid gases. Since CO and H_2 are soluble in cold methanol, Rectisol acid gases will also contain these constituents as well as traces of methanol vapor. Rectisol acid gases are by far the largest sources of uncontrolled sulfur and CO emissions in a K-T facility.

An additional acid gas stream is generated in conjunction with the cyanide wash operation preceding the acid gas removal unit. Flash gases from the cyanide wash are enriched in H_2S and HCN. In methanol-based cyanide wash systems, flash gases may also contain CO, COS, and methanol.

Approaches to treatment of the sulfur-rich acid gases are aimed primarily at removal of reduced sulfur species by bulk sulfur removal followed by tail gas treatment. Partial or essentially complete control of HCN, CO, NH_3, and methanol can be realized either as an integral part of the sulfur control approach or through a separate add-on step such as incineration. The approach for controlling CO emissions in sulfur-free acid gas streams involves incineration.

Bulk Sulfur Removal

To date only three processes have seen any significant commercial application for the removal of H_2S from acid or fuel gases, namely the Claus, Stretford, and Giamarco-Vetrocoke processes. These are the only processes examined here due to their commercial status, reliable operation, applicability to the wide range of sulfur contents in the acid gases, and, in the cases of the Claus and Stretford processes, availability of operating information and capital cost data. In addition to these processes, alternatives involving incineration with SO_2 removal may be applicable for facilities using low sulfur coals. It is recognized that a few other processes are available or have been proposed; however, it is unlikely that processes other than Claus, Stretford or Giamarco-Vetrocoke will be utilized in first generation coal gasification facilities in the U.S. In existing applications, Stretford units are favored economically over Claus units for feeds containing only a few percent sulfur, although Claus plants have operated successfully on feeds containing as low as 8% H_2S. The Giamarco-Vetrocoke process is generally applicable to feed streams with H_2S concentrations of up to 1.5%. Table 4-3 summarizes the key features of these bulk sulfur removal processes.

The Claus process is a dry, high temperature process in which H_2S is catalytically reacted with SO_2 to form elemental sulfur. There are two common versions of the process: "straight through", and "split flow". In the "straight through" mode, sufficient air is added to oxidize one-third of the H_2S to SO_2. The "split flow" mode, shown in Figure 4-1, is often used when H_2S levels in the feed gas are below 25% by volume. The acid gas is split into two streams and one-third of the input acid gas is combusted in a reaction furnace to form SO_2. Heat is recovered from the gas before it is recombined with the other two-thirds of the feed. The combined stream then enters a series of converter stages where elemental sulfur is produced. Regardless of the Claus mode, the number of stages determines sulfur removal efficiency; Claus units of 3-stage design can achieve overall

TABLE 4-3. KEY FEATURES OF BULK SULFUR REMOVAL PROCESSES

	Claus	Stretford	Giamarco-Vetrocoke (G-V)	Incineration/SO_2 Removal
Principle of Operation	Catalytic oxidation of H_2S and SO_2 to elemental sulfur.	Liquid phase oxidation of H_2S to elemental sulfur in an alkaline solution of metavanadate and anthraquinone disulfonic acid.	Liquid phase oxidation of H_2S to elemental sulfur in sodium carbonate and arsenate/arsenite solution.	Oxidation of reduced sulfur and organics, followed by SO_2 removal using either regenerative or throwaway FGD technologies.
Components Removed	H_2S, COS, RSH, VOC, NH_3, and HCN.	H_2S, HCN, and CH_3SH.	H_2S, COS, and CS_2.	H_2S, COS, RSH, VOC, and CO.
Efficiency	Over 95% total S, other combustibles partially destroyed.	As low as 1 ppmv H_2S but no removal of non H_2S sulfur.	99.99% H_2S removal.	As low as 100 ppmv VOC in incinerated gas and up to 99% total sulfur removal.
Feed Stream Requirements/ Restrictions	Streams containing H_2S levels much below 10% require enrichment prior to processing. Organics cause combustion control problems and "grey" sulfur.	High HCN loading should be reduced prior to processing to prevent excessive solution purge.	Maximum 1.5% H_2S in feed.	In principle, gases with any level of H_2S or sulfur compounds could be incinerated and subsequently treated via FGD. Other components cause no problem.
By-Products	Elemental sulfur.	Elemental sulfur.	Elemental sulfur which may require arsenic removal.	Either $CaSO_4$, concentrated SO_2, or throwaway lime sludges are generated by FGD units.
Secondary Waste Streams	Spent catalyst and catalyst regeneration decommissioning offgas.	Oxidizer vent gas and purge solution.	Oxidizer vent gas and arsenate/arsenite wash water.	Some condensate and scrubber sludge.
Reliability/ Limitations	NH_3 and HCs may cause catalyst plugging and variable sulfur recovery.	Process does not remove COS, RSH, or organics, HCN forms nonregenerable salts in scrubbing solution.	Hazardous nature of arsenic solution may cause handling and safety problems.	FGDs systems have varying degrees of reliability and generally have lower on stream factors than process units.
Effects of High CO_2 in Feed	Can adversely affect sulfur removal ability of the process.	High CO_2 concentrations will decrease absorption efficiency by lowering solution alkalinity. Increased absorber tower height and addition of caustic are required.	Little or no effect.	No effect except to increase energy requirement for incineration if insufficient combustibles are present in feed gas.
Capital Costs	\$25 to \$180 x 10^3 per Mg sulfur/day capacity depending on both total flow and sulfur content.	\$110 to \$270 x 10^3 per Mg sulfur/day capacity, depending primarily upon total flow.	No cost data available.	\$700 to \$1700 x 10^3 per Mg sulfur/day capacity depending upon total flow and degree of sulfur removal.
General Comments	Applicable only to acid gases from selective AGR system. Hydrocarbon removal from feeds may be necessary.	1 ppmv H_2S in tail gas is possible, however higher limits are proposed when high levels of other reduced sulfur species are present in tail gas.	Limited data available. Hazardous nature of arsenic solution makes application unlikely in large U.S. facilities.	FGD process has usually been applied to combustion flue gases containing less than 5000 ppmv SO_2 and achieving about 90% control. Performance and cost data for higher SO_2 feeds achieving 99% control are limited.

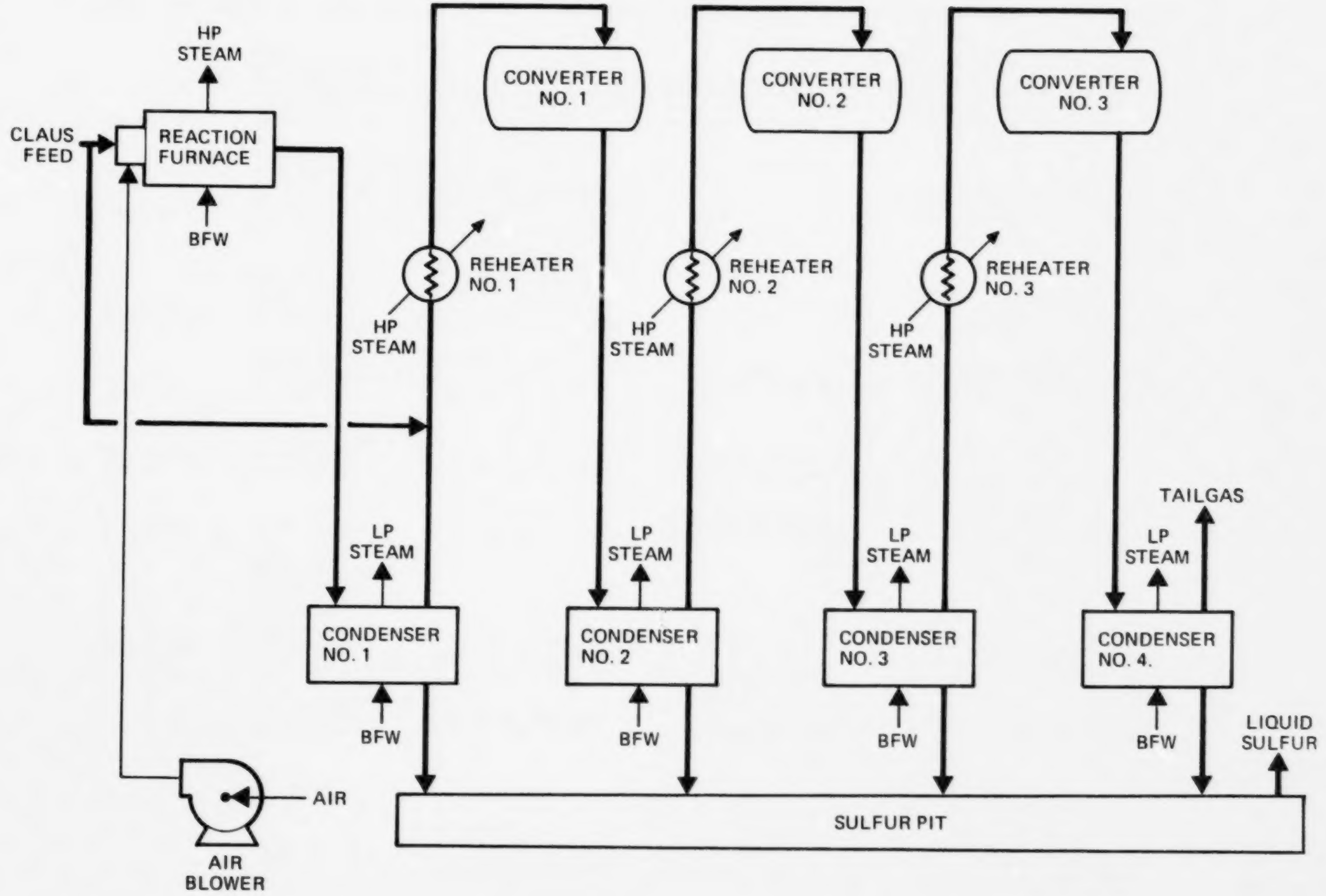

Figure 4-1. Three stage Claus plant with split flow option

removal efficiencies of over 95%. Gaseous sulfur species distribution in Claus tail gas in high CO_2 applications is approximately 60% H_2S, 30% SO_2, 9% COS, and 1% CS_2, although exact levels can vary depending upon the feed gas composition and Claus plant operation. Elemental sulfur as both vapor and entrained mist can contribute 20-50% to the total sulfur in Claus tail gases, depending primarily on the level of H_2S in the Claus feed and the effectiveness of mist eliminators. The relative contribution of elemental sulfur to total sulfur in Claus tail gas generally increases as H_2S content of Claus feed gas decreases.

In the "straight through" mode of Claus operation, organics, HCN, and NH_3 in the feed are largely converted to carbon dioxide, water vapor, and elemental nitrogen. Such components are not ordinarily of concern unless levels exceed perhaps 1% vol. each. Organics make control of combustion stoichiometry and temperature more difficult and can lead to an off-color byproduct sulfur containing elemental carbon. HCN at high levels causes corrosion throughout the process while NH_3 can form deposits which plug/deactivate Claus catalysts. The organics problem is usually solved by limiting their content in the Claus feed. HCN at high levels can be removed (converted to NH_3) prior to entering the Claus furnace using Claus or shift type catalysts under reducing conditions. Ammonia at high levels requires either bulk removal prior to entering the Claus unit or special design to minimize deposition of ammonia salts.

With feed gases dilute in H_2S or other combustibles, flame stability can be a problem in "straight through" operation. One method for control of the sulfur combustion process in Claus plants with feeds containing less than 25% H_2S or more than 30% CO_2 has been the use of the "split flow" mode. In this process, any organics, HCN, and NH_3 in Claus feed gases would be only about one-third destroyed in the split flow mode unless streams containing high levels of these constituents are specifically routed to the combustion furnace of the Claus plant. Generally, organics present the most difficult problem for split flow Claus plants, leading to carbon contaminated sulfur. A portion of the input organics, HCN, and NH_3 to split flow Claus plants may be present in Claus tail gases prior to incineration.

One problem potentially associated with "split flow" operation is the decomposition of olefins and aromatics to elemental carbon which contaminates the product sulfur. In such cases, other approaches to combustion control have been utilized. First, combustible gases such as CO, H_2, or CH_4 are added to the feed or are combusted separately to provide sufficient heat to enable operation in the straight through mode. Liquid sulfur has also been used. Second, and of particular attractiveness in coal gasification facilities, is the use of oxygen (O_2) or enriched air. Use of O_2 not only improves flame stability, but also decreases the inert volume through the Claus and any subsequent tail gas treatment units. Since unit sizes and associated costs are flow dependent, savings can be realized. Oxygen is expensive to generate, but much of the capital cost is already absorbed in a gasification facility which would necessarily have a large on-site oxygen plant. Finally, the acid gas and/or air can be preheated before being fed to the Claus burner, using steam or flue gas from fuel combustion as the heating media.

The Claus process produces spent catalyst and catalyst regeneration off-gases where catalyst regeneration is used. The Claus catalyst has an estimated life of at least two to three years. Regeneration of catalyst is performed intermittently at a few facilities when the efficiency of the process drops below acceptable levels. However, no data regarding regeneration frequency, duration, or offgas characteristics are available.

The original Stretford process (as developed by the British Gas Corporation) is a liquid-phase oxidation process using an aqueous solution of sodium vanadate and anthraquinone disulfonic acid (ADA) in which H_2S is both absorbed and converted to sulfur. Figure 4-2 is a simplified flow diagram of the Stretford process. The H_2S is absorbed in either a packed tower (or contacted in

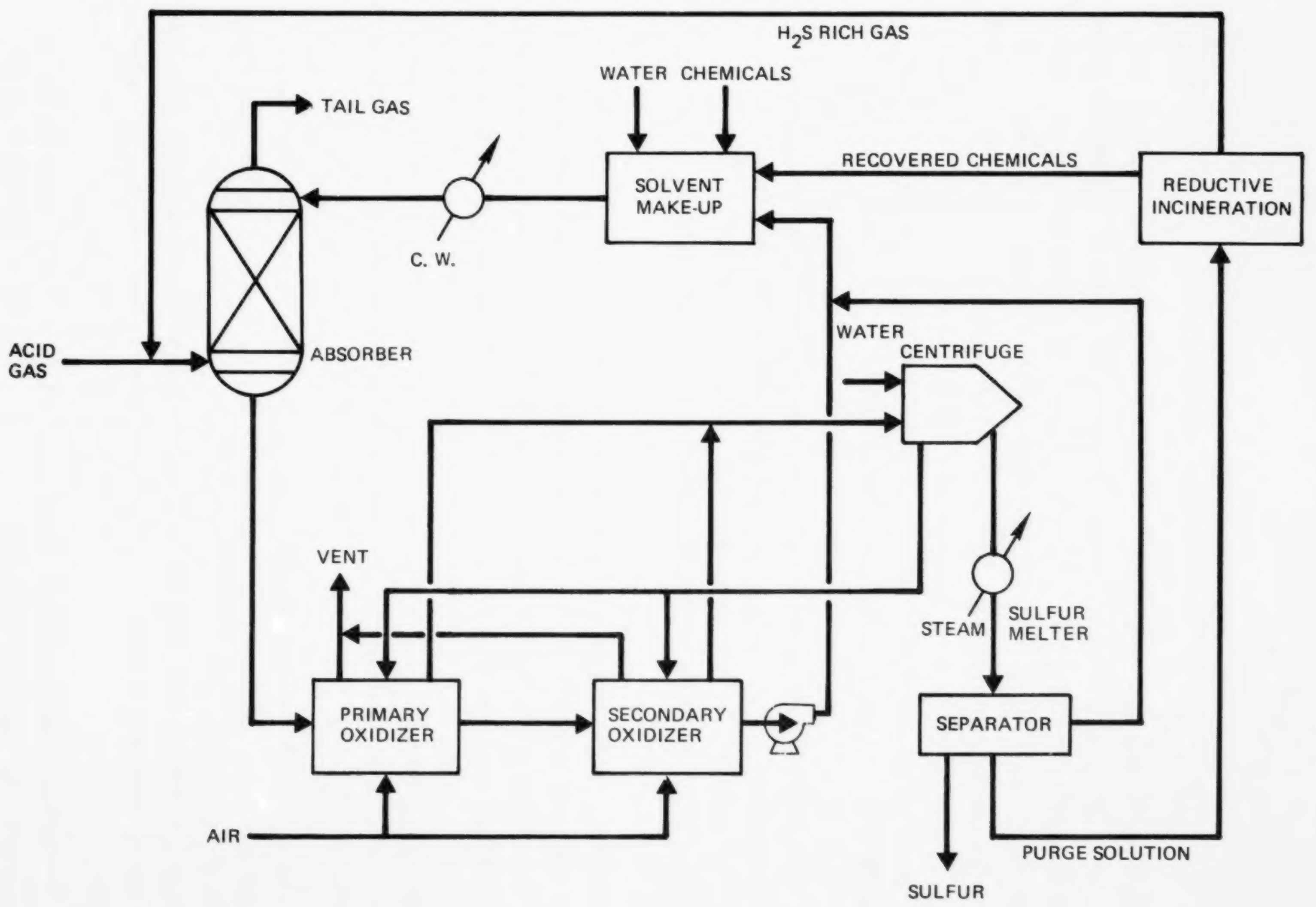

Figure 4-2. The Stretford process

a venturi scrubber) and then oxidized to sulfur by the sodium vanadate. Reduced vanadium is then oxidized by the ADA Solution. ADA is regenerated with air in the oxidizer tanks where elemental sulfur is removed as a froth. A continuous solution purge is required to remove the buildup of sodium thiosulfate and sodium thiocyanate. Until recently, disposal or treatment of the solution purge containing thiosulfate, thiocyanates, and small amounts of vanadium salts was required. In 1973, a reductive incineration process was developed which converts the purge solution into a gas stream containing H_2S, water vapor and a solid residue containing soda ash and reduced vanadium salts The salts are returned to the Stretford process as make-up chemicals and the H_2S-rich gas and water vapor are recycled to the absorber as shown in Figure 4-2. Thus, the reductive incineration process recovers expensive chemicals while effectively attaining a "zero" discharge of solution purge.

Recently, modifications of the original Stretford process have been developed. One modified version of the Stretford process has been used at the SASOL Lurgi coal gasification complex in South Africa. At SASOL, severe plugging problems have occurred in the Stretford towers which apparently relate to the high CO_2 levels in the Stretford feed compared to feeds in other services. Preliminary information indicates that sulfur deposition is primarily responsible. SASOL has modified the original Stretford unit, presumably substituting a different absorbent while saving the bulk of the existing equipment.

The Stretford process generates two waste streams, the oxidizer vent gas and the purge solution. The purge solution is treated via the reductive incineration process where sulfur is recovered as H_2S for recycle to the absorber and sodium and vanadium salts are recovered for reuse. The oxidizer vent gas is expected to consist primarily of air, carbon dioxide, and water vapor.

The Giamarco-Vetrocoke H_2S removal process is a liquid phase oxidation process using an absorbent solution of alkali arsenates/arsenites in which hydrogen sulfide is both absorbed and converted to elemental sulfur. Sodium carbonate is the alkali usually applied for removal of large quantities of sulfur because of its relatively low cost. The Giamarco-Vetrocoke process is applicable to gas streams containing up to 1.5% hydrogen sulfide and can reduce hydrogen sulfide levels to 0.5 ppmv or less. The hydrogen sulfide is absorbed at pressures from 0.1 to 7.5 MPa by countercurrent absorption. Rich solution from the absorber is subsequently oxidized in an atmospheric pressure, air-blown column to produce regenerated solution and elemental sulfur. Product sulfur is recovered by froth flotation, filtered, and washed. Based upon limited available data, the only waste streams generated by this process are wash water from the sulfur washing operation and oxidizer vent gas. Characterization data are not available for these streams although the wash water will contain arsenate/arsenite absorber solution.

In principle acid gases can be directly incinerated to convert all organics, CO, and reduced sulfur and nitrogen species to CO_2, H_2O, N_2 and SO_2. SO_2 removal from the incinerated gas could then be accomplished using any one of a number of available FGD processes (see Section 4.1.2). Generally, such an approach is unattractive for several reasons. Throwaway FGD systems create large solid waste disposal problems and recovery type FGD systems often feature Claus or Claus type (e.g., the Allied process) processes for elemental sulfur recovery. There is little to be gained in these approaches over direct use of the Claus process. FGD systems are also not demonstrated for gases containing over about 0.5% SO_2, and although there appear to be no inherent technical limitations prohibiting designs for much higher SO_2 levels, such systems are expected to be several times more costly than Claus or Stretford plants applied directly to crude acid gases. However, for facilities using very low sulfur coals, the direct incineration approach might be viable due to high costs associated with enrichment to obtain an H_2S-rich acid gas suitable for Claus processing.

Tail Gas Treatment

A number of processes are commercially available for treatment of sulfur plant tail gases or other waste gases containing low levels of reduced sulfur species. Table 4-4 summarizes the key features of the most prominent of these processes. The processes can be categorized in three generic types:

1) Conversion of sulfur species to H_2S followed by its removal - this includes processes such as the Beavon/Stretford and SCOT processes.
2) Conversion of sulfur species to sulfur dioxide (SO_2) by incineration, followed by SO_2 removal - this includes processes such as the Wellman-Lord or Chiyoda Thoroughbred 102.
3) Extensions of the Claus process - this includes processes such as the IFP-Clauspol 1500, Sulfreen or BSR/Selectox processes.

Processes in the first category involve catalytic reduction of oxidized sulfur species to H_2S followed by H_2S removal from the gas stream by solvent absorption. In general, the designs of these processes are influenced by the high levels of CO_2 in the feed gas. High CO_2 levels reduce the efficiency of catalytic reduction of COS and CS_2 to H_2S and impair the effectiveness of the H_2S removal/recovery systems.

Both the Beavon/Stretford and the SCOT processes are commercially available catalytic processes which are potentially applicable to sulfur plant tail gases in indirect coal liquefaction facilities. These processes feature two sections: a hydrogenation section to convert sulfur species in the gas to H_2S and an H_2S absorption section. In the hydrogenation reactor, a reducing gas is added to the feed gas and the combined gas stream is passed over a cobalt molybdate catalyst. The hydrogenation/hydrolysis reactions occur in the catalyst bed reducing the sulfur species to H_2S.

The Beavon process employs a Stretford unit for H_2S absorption and elemental sulfur production. In contrast, the SCOT process employs an alkanolamine scrubbing system for H_2S absorption. The absorbing solution is then regenerated resulting in a H_2S-rich acid gas which is ordinarily returned

TABLE 4-4. KEY FEATURES OF RESIDUAL SULFUR REMOVAL PROCESSES

	Beavon	SCOT	Incineration Plus SO_2 Removal (FGD)	Sulfreen
Principle of Operation	Catalytic reduction of sulfur compounds to H_2S, followed by integrated Stretford process.	Sulfur species are catalytically reduced to H_2S; H_2S is scrubbed in a regenerable amine system.	Incineration (an on-site boiler or separate incinerator) followed by SO_2 removal (e.g., Wellman-Lord).	Gas phase continuation of Claus reaction at a low temperature.
Components Removed	H_2S, COS, CS_2, and SO_2.	H_2S, COS, and CS_2, SO_2.	SO_2, also removes HCs, CH_3SH, NH_3, and HCN.	H_2S, SO_2, COS, and CS_2.
Efficiency	Over 99.9% total sulfur removal in combination with the Claus plant or can attain equivalent of 50 ppm total sulfur in tail gas (not including reducing gases).	Over 99.9% total sulfur removal in combination with the Claus plant or can attain equivalent of 250 ppm total sulfur in tail gas (will vary depending on CO_2 and H_2S concentration in specific applications).	Up to 99% total sulfur removal from Claus tail gas or 50 ppm SO_2 in tail gas and complete removal of other compounds.	Up to 99% sulfur removal in combination with Claus plant. Can expect a typical total sulfur level of 2500 ppm in tail gas.
Feed Stream Requirements/ Restrictions	None.	None.	None.	Optimum performance requires $H_2S:SO_2$ ration of 2:1.
By-Products	Elemental sulfur.	Concentrated H_2S.	Sulfur or sulfuric acid from the Wellman-Lord recovery FGD process.	Elemental liquid sulfur.
Secondary Waste Streams	Sour condensate, oxidizer vent gas, solution purge, and spent catalyst.	Sour condensate and spent catalyst.	Sour condensate and solution purge.	Spent catalyst.
Reliability/ Limitations	Has only been applied to Claus process tail gases.	Requires further treatment and/or recycle to Claus.	Solid wastes may be generated by throwaway FGD processes.	Has only been applied to Claus process tail gases.
Effects of High CO_2 in Feed	Reduces conversion efficiency of catalyst and decreases H_2S absorption in Stretford solution.	Reduces conversion efficiency of catalyst and efficiency of alkanolamine system.	None.	No effect.
Capital Costs	\$20 to \$60 x 10^3 per Mg/day of S at Claus plant.	\$20 to \$60 x 10^3 per Mg/day of S at Claus plant.	\$40 to \$110 x 10^3 per Mg/day of S at Claus plant.	
General Comments	Exact ppm limit achievable in coal gasification application is not known. Vendor believes 100 ppm is attainable.	Off-gas from amine scrubber is not as low in total sulfur as Beavon process.	On-site boiler/FGD system is the most likely candidate Installing a separate incinerator and FGD would not be as economically feasible.	Much higher residuals in tail gas than Beavon process.

(Continued)

TABLE 4-4. (CONTINUED)

	Cleanair	IFP Claus 1,500	IFP-2	BSR/Selectox
Principle of Operation	Catalytic reduction of sulfur compounds to H_2S followed by a continuation of the Claus reaction and Stretford process.	Liquid phase continuation of Claus reaction at a low temperature.	Incineration of tail gas followed by ammonia scrubbing. Solution is evaporated to produce a concentration SO_2 stream which is returned to the Claus plant.	Catalytic reduction of sulfur compounds to H_2S, followed by oxidation of H_2S to sulfur over Selextox catalyst.
Components Removed	H_2S, COS, CS_2, and SO_2.	H_2S, and SO_2.	COS, CS_2, and H_2S.	H_2S, SO_2, COS, and CS_2.
Efficiency	Reduces sulfur to less than 250 to 300 ppm SO_2 equivalent in effluent.	Reduces sulfur species in Claus tail gas to 1500 ppm as SO_2.	Reduces sulfur species in Claus tail gas to less than 500 ppm.	Up to 99.5% total sulfur removal equivalent to 750 ppmv SO_2 in the incinerated off-gas.
Feed Stream Requirements/ Restrictions	$H_2S:SO_2$ ratio can vary up to 8 to 1 without affecting efficiency; designed specifically for Claus tail gas.	$H_2S:SO_2$ ratio must be maintained in the range of 2.0 to 2.4.	$H_2S:SO_2$ ratio must be maintained in the range of 2.0 to 2.4.	$H_2S:SO_2$ ratio must be maintained in the range of 2.0 to 2.4. HC and NH_3 should not be in the feed.
By-Products	Elemental sulfur.	Elemental sulfur.	Concentrated SO_2.	Elemental liquid sulfur.
Secondary Waste Streams	Spent catalyst.	Spent catalyst.	Spent catalyst.	Spent Beavon and Selectox catalyst, and sour condensate.
Reliability/ Limitations	Has only been applied to Claus process tail gases.	Has only been applied to Claus process tail gases.	Has only been applied to Claus process tail gases.	Has only been applied to Claus plant tail gas.
Effects on High CO_2 in Feed	Reduces conversion efficiency of catalyst; decreases H_2S absorption in Stretford solution.	No effect.	No effect.	Reduces conversion efficiency of BSR catalyst.
General Comments	Cannot attain as low a residual sulfur level in tail gas as Beavon process.	Cannot attain as low a residual sulfur level in tail gas as Beavon process.	Cannot attain as low a residual sulfur level in tail gas as Beavon process.	Higher sulfur emissions than Beavon process.

to the parent Claus plant for treatment. The alkanolamine scrubbing system ultimately limits the SCOT's capabilities because the solvent is only partially selective for H_2S over CO_2. Thus, where feeds contain large amounts of CO_2, it is more difficult to generate an H_2S stream suitable for Claus processing while simultaneously obtaining a tail gas stream with a low level of total sulfur. In high CO_2 applications, vendors of the Beavon process report that levels of less than 100 ppmv total sulfur can be achieved, while vendors of the SCOT process report less than 350 ppmv total sulfur (Claus plant tail gas bases).

Inherent limitations of selectivity in the amine absorption step of the SCOT process place a lower limit of about 200 ppmv of H_2S which will be present in SCOT tail gases. In comparison, the Stretford unit following the Beavon reactor can remove H_2S to below 10 ppmv H_2S. Both systems would result in 50-100 ppmv tail gas COS in high CO_2 applications. The higher levels of H_2S in SCOT tail gases in existing applications have necessitated that the gases be incinerated to minimize odor problems while Beavon tail gases do not generally require incineration. However, no Beavon/Stretford units are currently used in high CO_2 service, while at least four SCOT units have sucessfully operated on feeds with CO_2 levels above 40%.

The secondary category of processes involves incineration of the waste gas followed by SO_2 removal. Such processes are capable of achieving levels as low as 150 ppmv of SO_2 in tail gas. One of the more prominent processes, the Wellman-Lord process, removes SO_2 with a sodium sulfite solution. Subsequent regeneration of the absorbent generates a concentrated SO_2 stream which would be recycled to the parent Claus plant. Two approaches to incineration can be employed, either separate incineration (with added fuel where needed) or incineration in an onsite boiler. Either option would net similar results from a sulfur oxidation standpoint.

Processes in the third category are used exclusively for Claus plant tail gases and are capable of approximately 80% recovery of tail gas sulfur.

These processes are extension of the Claus process and therefore require a 2:1 ratio of H_2S to SO_2 for proper operation. The limited sulfur removal capabilities of these processes result in sulfur concentrations of not less than 1000 ppmv. To date, these processes have not been proposed for coal gasification applications in the U.S.

Incineration

As discussed above, partial or total control of HCN, CO, NH_3, and VOC can be achieved during bulk sulfur removal or sulfur tail gas treatment. The combustion section of a Claus unit largely destroys these constituents, but only in that portion of the gas passing through the burner. Cyanide can also be destroyed over Claus type catalysts used ahead of the Claus plant itself. HCN is removed from feed gases in the Stretford process, forming SCN^- which leaves the systems with the aqueous blowdown. NH_3 is also partially removed by Stretford solvent while organics, CO, and COS are not removed by Stretford. Catalytic sulfur tail gas treatment systems achieve at least partial control of any residual HCN contained in sulfur plant tail gases. Both Beavon and SCOT catalytic sections are expected to achieve a high degree of conversion of HCN to NH_3 and CO. Hydrocarbons, CO, and NH_3 contained in the feed to Beavon or SCOT units or added/generated within such units will be present in their tail gases.

Incineration of these tail gases is an effective approach to controlling residual hydrocarbons, CO, NH_3, and reduced sulfur species. In addition, incineration is essentially the only alternative for controlling CO emissions associated with CO_2-rich acid gases. SCOT tail gases are ordinarily incinerated to minimize odor problems arising from residual H_2S. Beavon tail gases (with lower H_2S levels) are not ordinarily incinerated, but an incineration step can be added for control of organics, CO, and/or NH_3 if necessary. Sulfur dioxide tail gas treatment processes such as the Wellman-Lord inherently achieve control of VOC, CO, and NH_3 as part of the incineration step. Hence, no further control for these constituents is ordinarily necessary with SO_2 removal processes.

Advantages and disadvantages of the various incineration technologies aimed primarily at control of volatile organic compounds are summarized in Table 4-5. Generally, a greater degree of control is obtained with high

TABLE 4-5. COMPARISON OF INCINERATION PROCESSES

Type of Incineration	Advantage	Disadvantage	Costs (Total Depreciable Capital)
Thermal Incineration via Separate Incinerator	Can handle all types of waste gases. Reliable and simple operation is common. VOC/CO control and oxidation of sulfur compounds simultaneously.	High supplemental fuel costs for streams with low heating value, control is a problem with streams of varying flow and composition.	On basis of kmols/hr of flow: flow range of 0.3 to 3.0 x 10^3 kmol/hr a. no heat recovery: $140 to $870 b. primary heat recovery: $190 to $1000 c. primary and secondary heat recovery: $225 to $1200
Thermal Incineration in Fuel Fired Boiler	Sulfur and particulates can be removed in the associated electrostatic precipitator and flue gas desulfurization (FGD) units when these are integral with the boiler. The fuel required for steam boiler incineration is less than that of a separate incinerator for wastes with low heating values.	In most cases, this option is more capital intensive than a separate incinerator; however, extent of heat recovery is generally greater with boilers than with incinerators. Subject to control problems with varying waste gas flow rates and compositions.	Incremental boiler capital costs are $2000-$3000/kg mole of incremental flue gas compared to coal combustion on a heating value basis. Incremental ESP and FGD costs are an additional $2000-$2500/kg mole incremental flue gas.
Catalytic Incineration	Requires less fuel than thermal incineration, although heat recovery may not be as high. Waste gases with very little combustible material can often be incinerated catalytically without supplemental fuel.	Cannot handle large quantities of particulates; they will gradually coat the catalyst and reduce its efficiency. Some catalyst can be easily poisoned by sulfur compounds and elements such as arsenic and lead. High levels of hydrocarbons can raise catalyst to excessive temperatures and shorten the useful life of the catalyst. Temperature control is also a problem with streams of varying flow and composition.	$400 to $2200 per kmol/hr of flow for a flow rate range of 40 to 7100 kmol/hr
Flaring	Simple to operate, least expensive alternative, especially for transient and small volume waste gases.	Destruction efficiencies much lower than for thermal or catalytic incineration. Performance data are generally lacking.	• 40 to 100 ft elevated flares for flow rate range of 800 to 6500 kmol/hr - $25 to $125 per kmol/hr • Ground flares for flow rate of 100 to 1000 kmols/hr - $800 to $2700 per kmol/hr

temperature incineration in either a fuel-fired boiler or a separate incinerator (either thermal or catalytic) than can be achieved through the use of flares. The main combustion zone of a gas incinerator is engineered such that the gases are maintained at a minimum temperature of 1100K for a minimum of 0.5 seconds. This results in nearly complete destruction of volatile organic compounds, reduced sulfur compounds, organic aerosols, CO, NH_3, HCN, and particulate matter consisting primarily of combustible material.

Thermal incineration may also be effected in a boiler where a minimum combustion temperature of 1500K and a minimum residence time of 0.5 seconds are typical design parameters. This approach results in a degree of pollutant destruction similar to that which would be achieved in a specially engineered incinerator. In tail gas or CO_2-rich offgas treatment applications, using the boiler as an incinerator results in an increase in the capital and annualized operating costs of captive ESP and FGD units, since costs of the pollution control units are flow rate dependent (even if the increased gas flow to the ESP/FGD unit contains no dust or sulfur dioxide), and these waste gases will not be of sufficient heating value to displace the primary boiler fuel.

Catalytic incineration is not likely to be an attractive alternative for control of carbon monoxide and VOC in tail gases from sulfur recovery units due to the presence of sufficient reduced sulfur compounds to interfere with or degrade catalysts. However, catalytic incineration of CO-rich flash gases from Rectisol has considerable promise, and is featured in the recent design of at least one U.S. coal gasification facility under construction (based on Texaco gasification).

4.1.1.1 H_2S-Rich Rectisol Offgas (Stream 216) - Individual Stream Control

Details of pollution control alternatives applicable to the H_2S-rich Rectisol offgas (Stream 216) are discussed in this section. Although this discussion focuses primarily upon individual stream controls, the cost estimates provided reflect the fact that, in a K-T based gasification facility, H_2S-rich Rectisol offgas would most probably be combined with the relatively small volume cyanide wash flash gases (Stream 214) prior to treatment. The likelihood of such stream combination derives from the high sulfur concentrations of both of these streams, and the high percentage of the gasified coal total sulfur present in the cyanide wash flash gases (about 1 to 3%). This approach is necessary in order to provide realistic cost estimates for the bulk sulfur removal, tail gas treatment, and incineration controls discussed in this section.

For evaluation purposes, the H_2S-rich Rectisol offgas have been assumed to contain 50% carbon dioxide, 42% hydrogen sulfide, 5% carbonyl sulfide, 0.4% carbon disulfide, 636 ppmv cyanide, and 200 ppmv sulfur dioxide. The main organic compound present in significant quantities is expected to be methanol at about a 1% level (see Section 3.3.6). The corresponding flow rate for this stream is about 535 kmol/hr. It should be noted that the exact hydrogen sulfide level in the H_2S-rich Rectisol offgas would be determined based upon engineering/economic tradeoff studies of Rectisol enrichment costs versus bulk sulfur removal and tail gas treatment costs. The most economic sulfide level is likely to be coal-specific and, in particular, vary with coal sulfur content and sulfur recovery/pollution control alternatives.

Bulk Sulfur Removal

In the base plant, the H_2S-rich Rectisol offgas contains approximately 255 kmol/hr total sulfur, and is the primary feed gas to the bulk sulfur removal unit. An additional 2 to 8 kmol/hr of total sulfur is likely to be present in the feed gas to bulk sulfur removal, depending upon whether a water-based or methanol-based cyanide wash system is employed (refer to Sections 3.3.4 or 4.1.1.2 for cyanide wash flash gas compositions). Thus, a total feed rate to the bulk sulfur removal unit of about 549 kmol/hr, including 257 to 263 kmol/hr total sulfur (approximately 47% total sulfur), is expected from the uncontrolled base plant. Such a stream is suitable for bulk sulfur removal by the Claus process since it has a relatively high sulfur concentration and does not contain appreciable levels of contaminants such as organics, HCN, or NH_3.

As discussed previously, Claus units of 3-stage design can achieve overall sulfur removal efficiencies of over 95%. Assuming a 95% sulfur removal efficiency, a Claus tail gas sulfur loading of 13 kmol/hr would be expected. The gaseous sulfur species distribution in Claus tail gas in high CO_2 applications is approximately 60% H_2S, 30% SO_2, 9% COS, and 1% CS_2. It should be noted that up to 50% of the Claus tail gas total sulfur (SO_2 equivalent basis) may actually be present as either sulfur vapor or entrained elemental sulfur. However, this would not appreciably alter the tail gas sulfur species distribution (e.g., for 50% SO_2 equivalent sulfur as S_8, the species distribution would become 53% H_2S, 27% SO_2, 8% COS, 1% CS_2, and 11% S_8). The corresponding concentration of total sulfur (SO_2 equivalent) in the Claus tail gas would be 1.5 to 1.6% (dry basis). Some degree of removal of minor constituents present in the Claus feed gas such as methanol, CO, and HCN would be achieved in addition to sulfur removal. It is expected that about one-third or more of the methanol and CO present in the feed gas would be combusted resulting in tail gas concentrations of less than 0.6% and 0.4%, respectively. However, CO is apparently generated within the Claus reactor, and concentrations of CO in the 1 to 2% range are typically reported. Feed gas cyanide, present at concentrations of up to about 0.4%, is expected to be almost totally destroyed during Claus processing but may contribute to low levels of NH_3 in the tail gas. For the subject Claus plant, a dry tail gas flow rate of about 800 to 900 kmol/hr would be expected with 200 to 250 kmol/hr of reaction moisture.

For a Claus plant of the capacity specified above, total capital investment and annualized costs would be about $8.7 million and $0.4 million, respectively. However, the cost of the Claus unit is dependent upon both the feed gas flow rate and sulfur content. For example, if the selectivity achieved by the Rectisol unit was reduced to produce a Claus feed gas with 15% sulfur for the same coal sulfur content, the Claus feed gas rate would increase by a factor of about three and the total capital investment for the Claus plant would increase by about 40%. Alternatively, with the same Rectisol selectivity (i.e., 47% sulfur in the Claus feed) for a feed coal having one-half the total sulfur content initially considered, the Claus feed rate would decrease by about one-half and the total capital investment for the Claus plant would decrease by about 40%.

The principal secondary waste stream generated by the Claus process is spent catalyst (Stream 402). The subject Claus plant would have a bauxite or alumina catalyst inventory of approximately 50 Mg which would periodically require disposal. Assuming a catalyst life of 5 years, the average spent catalyst generation rate would be 10 Mg per year. Claus sulfur is produced at a rate of approximately 7.9 to 8.3 Mg/hr and may also require disposal depending upon its quality and market considerations.

Tail Gas Treatment

In the base plant, tail gas from bulk sulfur removal would contain approximately 1.5% total sulfur and less than 0.6% methane and 1 to 2% CO, on a dry gas basis. Traces of NH_3 may also be present as a result of HCN destruction during bulk sulfur removal. A tail gas flow rate of about 840 kmol/hr dry gas and 300 kmol/hr water vapor is expected. A number of processes are available for recovering residual sulfur from tail gases from bulk sulfur removal processes (refer to Section 4.1.1). For purposes of discussion, the Beavon/Stretford, SCOT, and Wellman-Lord processes will be considered.

The Beavon/Stretford process is reported to be capable of reducing residual sulfur concentrations to about 100 ppmv (dry tail gas basis) with a 9:1 ratio of COS to H_2S. This corresponds to a total sulfur emission rate of less than 0.1 kmol/hr from tail gas treatment. Minor constituents such as methanol and NH_3 present in the tail gas from bulk sulfur removal are not expected to be affected by the Beavon/Stretford process. An external source of reducing gas may be required for the catalytic hydrogenation of SO_2 and elemental sulfur. Reducing gas may be added directly to tail gas treatment in the form of H_2 and CO-rich gas (e.g., flash gases from Rectisol) or may be generated by substoichiometric combustion of organic-rich fuel gas derived from synthesis operations. The extent to which this reducing gas dilutes the residual sulfur concentration from tail gas treatment depends upon the reducing gas quality and the amount of air required for stable combustion. For this reason, performance of Beavon/Stretford units is typically reported on a dry tail gas basis. Residual reducing gas will contribute to CO concentrations in the effluent from the Beavon/Stretford process although quantitative data are not available. The total capital investment and annualized costs of the subject Beavon/Stretford unit would be approximately \$7.4 million and \$1.4 million, respectively.

Secondary waste streams from the Beavon/Stretford process are: (1) sour reactor effluent condensate (Stream 405), (2) Stretford solution purge (Stream

406), (3) Stretford oxidizer vent gas (Stream 404), and (4) spent catalyst from the Beavon reactor (Stream 407). Sour condensate is expected to contain dissolved sulfide and traces of NH_3, and would be generated at a rate of up to 4 m^3/hr. Stretford solution purge for control of thiosulfate and thiocyanate buildup may be present as a waste stream containing vanadium and sodium salts as thiosulfate, sulfate, carbonate, and thiocyanate. The solution purge rate is approximately 0.1 to 0.2 Mg/hr and purge solution may either be regenerated or discarded (refer to Section 4.1.1). Oxidizer vent gas would consist primarily of air, water vapor, and CO_2 but may contain traces of NH_3. Insufficient data are available for estimating the flow rate of oxidizer vent gas. The cobalt molybdate hydrogenation catalyst inventory is approximately 15 Mg and would require periodic replacement. Assuming a catalyst service life of three years, the average spent catalyst generation rate would be 5 Mg/year. Beavon/Stretford sulfur is generated at a rate of approximately 0.4 Mg/hr and may require disposal, depending upon its quality and market considerations.

The SCOT process is reported to be capable of reducing residual sulfur concentrations to about 250 ppmv (dry tail gas basis). This corresponds to a total sulfur emission rate of 0.2 kmol/hr from tail gas treatment. Minor constituents such as methanol and NH_3 present in the tail gas from bulk sulfur removal are not expected to be affected by the SCOT process. As discussed in conjunction with the Beavon/Stretford process, supplemental reducing gas would be required, and the reducing gas quality/generation mode would influence the concentration of sulfur species in the tail gas treatment effluent but not the sulfur effluent rate. Residual reducing gas will contribute to CO concentrations in the treated gas from the SCOT process although quantitative data are not available. The total capital investment and annualized costs of the subject SCOT unit would be approximately \$6.3 million and \$1.9 million, respectively.

Secondary waste streams from the SCOT process are sour water (Stream 409) and spent catalyst (Stream 410). The sour water is expected to contain dissolved sulfide and traces of NH_3, and would be generated at a rate of 5 m^3/hr. The cobalt molybdate hydrogenation catalyst inventory is approximately 15 Mg, and would require periodic replacement. Assuming a catalyst service life of 5 years, the average spent catalyst generation rate would be 3 Mg/year.

The Wellman-Lord process is reported to be capable of reducing residual sulfur concentrations to about 250 ppmv SO_2 (dry tail gas basis). This corresponds to a total sulfur emission rate of 0.2 kmol/hr from tail gas treatment. Minor constituents such as methanol, CO, and NH_3 present in the tail gas from bulk suflur removal are expected to be destroyed during tail gas incineration. Combustion of the tail gas requires supplemental fuel and air, and results in an increase in the molar flow rate through the tail gas treatment unit. The magnitude of this increase and its related SO_2 dilution depend upon the quality of the supplemental fuel and the stoichiometric excess of air. Assuming methane as the incineration fuel with 20% excess air, effluent from the subject Wellman-Lord unit would contain about 150 ppmv SO_2. The total capital investment and annualized costs for this Wellman-Lord unit would be approximately $11 million and $3.7 million, respectively.

Secondary waste streams from the Wellman-Lord process are acidic wastewater from combustion gas quenching (Stream 411) and thiosulfate/sulfate by-product purge (Stream 412). The acidic wastewater typically has a pH value between 1 and 2, and would be generated at a rate of 3 m^3/hr. By-product purge consists primarily of sodium salts such as sulfite, pryosulfite, sulfate, and thiosulfate with approximately 29% water. By-product purge is generated at a rate of 90 kg/hr.

Incineration

Waste gases from tail gas treatment may be incinerated to control odors due to the presence of H_2S and to destroy CO. As discussed in Section 4.1.1, thermal incineration, catalytic incineration, and flaring are employed in various commercial applications. Thermal incineration in a dedicated incinerator is an approach often used in conjunction with tail gas treatment units and will be considered in this section.

In the base plant, gases from tail gas treatment processes not having an integral incineration step are generated at a rate of approximately 880 kmol/hr. The sulfur content of these gases ranges from 100 to 250 ppmv with H_2S concentrations ranging from 10 to 200 ppmv. The level of combustibles is expected to be inadequate to support combustion, and supplemental fuel would be required for incineration. Using desulfurized, unshifted synthesis gas as a typical fuel and an incineration temperature of 1100K, about 1230 to 1300 kmol/hr of incineration gas would be generated. The concentration of SO_2 in the effluent would be 70 to 180 ppmv, depending upon the input sulfur concentration and the amount of excess combustion air provided for incineration. Concentrations of CO in the combustion gas are likely to be below 100 ppmv although quantitative data are limited. No secondary waste streams are generated by thermal incineration processes. The total capital investment and annualized costs for the subject thermal incinerator would be approximately $0.42 million and $0.63 million, respectively.

4.1.1.2 Cyanide Wash Flash Gases (Stream 214) - Individual Stream Control

Generation rates and compositions of flash gases from cyanide wash operations are dependent upon whether a water-based or methanol-based cyanide wash is employed (see Section 3.3.4). In the case of a water-based cyanide wash, the estimated flash gas generation rate is 22 kmol/hr, consisting of 89% CO_2, 11% H_2S, and 449 ppmv HCN (Stream 214a). In the case of a methanol-based cyanide wash, the estimated flash gas generation rate is 16 kmol/hr, consisting of 45% H_2S, 27% CO, 13% HCN, 7% CO_2, 3% COS, and 2% methanol (Stream 214b). Due to the relatively high sulfur concentrations of these streams and since they may contain 1 to 3% of the gasified coal's total sulfur, these gases would probably be treated in bulk sulfur removal with the larger volume H_2S-rich Rectisol offgas (Stream 216). Control of cyanide wash flash gases would be achieved as previously discussed in conjunction with controls applicable to the H_2S-rich Rectisol offgas (Section 4.1.1.1).

4.1.1.3 CO_2-Rich Rectisol Offgas (Stream 219) - Individual Stream Control

For purposes of analyses, the combined CO_2-rich Rectisol offgas (Stream 219) has been estimated to consist primarily of CO_2 with 13 ppmv total sulfur and 1% CO (see Section 3.3.6). The indicated sulfur level in this stream is below the levels attainable with existing sulfur removal processes, and no further treatment for sulfur removal is warranted. In the event that CO control would be required for this stream, the Rectisol unit could be designed to further reduce the CO concentration. Carbon monoxide is sparingly soluble in methanol, and CO absorbed from K-T product gas at high pressures can be largely recovered as a separate CO-rich CO_2 stream by flashing laden methanol from CO_2 absorption to an intermediate pressure before regeneration for bulk CO_2 removal. The CO-rich offgas can be subsequently incinerated for control of CO emissions; this approach has been proposed in the U.S. for one Texaco-based coal gasification facility employing the selective Rectisol process. Alternatively, the CO-rich offgas may be recompressed for addition to the Rectisol product gas if the resulting CO_2 load is compatible with synthesis requirements. This latter alternative may involve design modifications for both the shift conversion and CO_2-removal operations to ensure an appropriate synthesis gas composition. Finally, the CO-rich offgas may be utilized within the facility as either fuel or reducing gas. Any of these alternatives would offer advantages over "add on" control of CO in the combined CO_2-rich offgas stream due to the energy penalty associated with incineration of high volume, low heating value gases.

With regard to controlling potential CO emissions associated with the CO_2-rich Rectisol acid gas, catalytic incineration of a CO-rich offgas will be examined in this section. It should be noted that constraints associated with the control of CO emissions would influence the design of the Rectisol acid gas removal unit and, possibly, the shift conversion unit. This influence may result in an increased cost for these units which should be attributed to pollution control. However, due to the absence of specific design and cost information for the Rectisol and shift conversion units, these costs will not be addressed in this section. Therefore, control costs presented in this section may be lower than the actual cost incurred in an integrated facility.

Incineration

To evaluate catalytic incineration as a CO control alternative, a CO-rich CO_2 stream containing 20% CO and 80% CO_2 has been assumed to be obtainable from the Rectisol unit. The flow rate of this stream would be approximately 500 kmol/hr. No supplemental fuel is required for incineration of this waste gas in a catalytic incinerator. With a 99% combustion efficiency, CO emissions from the incinerator would be 1 kmol/hr at an effluent concentration of about 1000 ppmv. The total capital investment for this catalytic incinerator would be approximately $574,000 which corresponds to 0.05% of the base plant capital investment. The associated annualized capital charge is offset by steam credits from heat recovery and a net annualized credit of $54,000 results.

4.1.1.4 Secondary Streams from Other Media

As will be discussed in Section 4.2.4, certain volatile species may degas or be stripped from wastewaters during treatment. This problem is most likely to occur with the polysulfide addition and activated sludge processes. The mass flow of volatile species in the offgas is uncertain, but is expected to be quite low, and volatiles would primarily consist of hydrogen sulfide with lesser amounts of hydrogen cyanide and ammonia. Such fugitive emissions would primarily represent a potential odor problem.

If control of volatile emissions (sulfide/cyanide offgas - Stream 416) from water pollution control operations is warranted, incineration may be a viable destruction alternative. One approach to control would involve providing air-blanketed enclosures for water pollution control units which may emit odorous volatiles. The enclosure vent gas could then be used as combustion air in on-site incinerators or boilers. Such an approach would obviate the need for a dedicated incineration unit, but would require the purchase and maintenance of enclosures, fans, and ducting. Control costs would primarily depend upon factors such as the specific water pollution control units requiring control, the location of the incineration unit(s) best suited for such an application, and the purge rate of blanketing air required to maintain slightly subatmospheric pressures within the water pollution control enclosures.

Enclosure of activated sludge units with induced draft collection of overhead gases for incineration is practiced at a number of domestic/industrial sewage treatment plants in the U.S. These treatment plants are generally much larger than those which would be found in K-T based facilities; therefore, induced draft collection appears feasible from both an economic and technical standpoint. Large ponds which might be utilized in K-T facilities as "polishing" steps would be difficult to enclose. However, most volatiles would evolve from upstream treatment units which could be more economically enclosed. Costs associated with control of volatile species from wastewater treatment operations will not be addressed in this manual due to large uncertainities in emissions, their sources, and the site/design-specific nature of costing factors.

4.1.1.5 Integrated Control Examples

In this section, examples of combined and sequential control of waste streams are evaluated from the standpoint of the overall emissions reductions achieved and costs incurred. The selection of specific control examples for evaluation in this section is not intended to imply that other technologies could not provide equivalent or better performance with similar or even lower costs. Specific technologies are selected to cover the types of alternatives which are under consideration for facilities in the U.S. Selection of integrated controls will be based upon specific design requirements and local conditions and can only be made by designers and regulatory authorities involved in a specific project.

Acid gas streams containing reduced sulfur/nitrogen compounds, organics, and CO and which would logically be combined prior to sequential control treatment are the H_2S-rich Rectisol offgas (Stream 216) and the cyanide wash flash gases (Stream 214). Three sequential control alternatives for the combined waste gas stream will be examined in this section.

- Claus bulk sulfur removal with Beavon/Stretford tail gas treatment
- Claus bulk sulfur removal with SCOT tail gas treatment, and incineration
- Claus bulk sulfur removal with Wellman-Lord tail gas treatment

These alternatives have been demonstrated in refinery applications and are currently under consideration for application to the North Alabama Coal Gasification Consortium Project (82). Detailed descriptions of the controls included in these alternatives are presented in the PCTM Pollution Control Technology Appendices.

Example 1 - Claus Bulk Sulfur Removal with Beavon/Stretford Tail Gas Treatment

This example illustrates treatment of the combined H_2S-rich Rectisol offgas (Stream 216) and the flash gas from a methanol-based cyanide wash unit (Stream 214b) in a Claus bulk sulfur removal unit with Beavon/Stretford tail gas treatment. The control system is presented schematically in Figure 4-3, and material flow estimates are presented in Table 4-6. The Claus process could operate in either a "split flow" mode, with the cyanide-rich flash gas passing entirely through the burner for HCN destruction, or in a "straight through" mode. The sulfur concentration of the combined feed gas (47% total sulfur) is sufficiently high to enable "straight through" processing. Also, the HCN level of 0.4% in the combined feed gas is not expected to require special approaches for HCN destruction.

The Claus unit is reported to achieve 95% sulfur removal and have a residual sulfur distribution of 60% H_2S, 30% SO_2, 9% COS, and 1% CS_2. It should be noted that up to 50% of the residual sulfur (SO_2 equivalent basis) may actually be present as either sulfur vapor or entrained elemental sulfur, which would slightly reduce the tail gas volume. One-third of the feed gas CO and methanol have been assumed to be destroyed during Claus processing, although higher methanol destruction efficiencies may result depending upon the specifics of the combustion process. Carbon monoxide may actually be generated in the Claus process since some facilities report tail gas concentrations of 1 to 2% CO with essentially CO-free Claus feed gases. Complete HCN destruction has been assumed; some low level NH_3 emission may result from HCN destruction although quantitative data are not available.

The Beavon/Stretford unit is reported to be capable of reducing tail gas residual sulfur concentrations to about 100 ppmv (dry Claus tail gas basis) with a 9:1 ratio of COS to H_2S. A CO-rich fuel gas has been used in the example for reheat of the Claus tail gas and catalytic reduction of SO_2. The resulting sulfur emission rate is 0.08 kmol/hr from tail gas treatment. Methanol present in the Claus tail gas is not expected to be affected by the Beavon/Stretford process. While no residual reducing gas in the Beavon effluent has been indicated in Table 4-6, concentrations of CO ranging from 250 to 670 ppmv in the effluent have been reported.

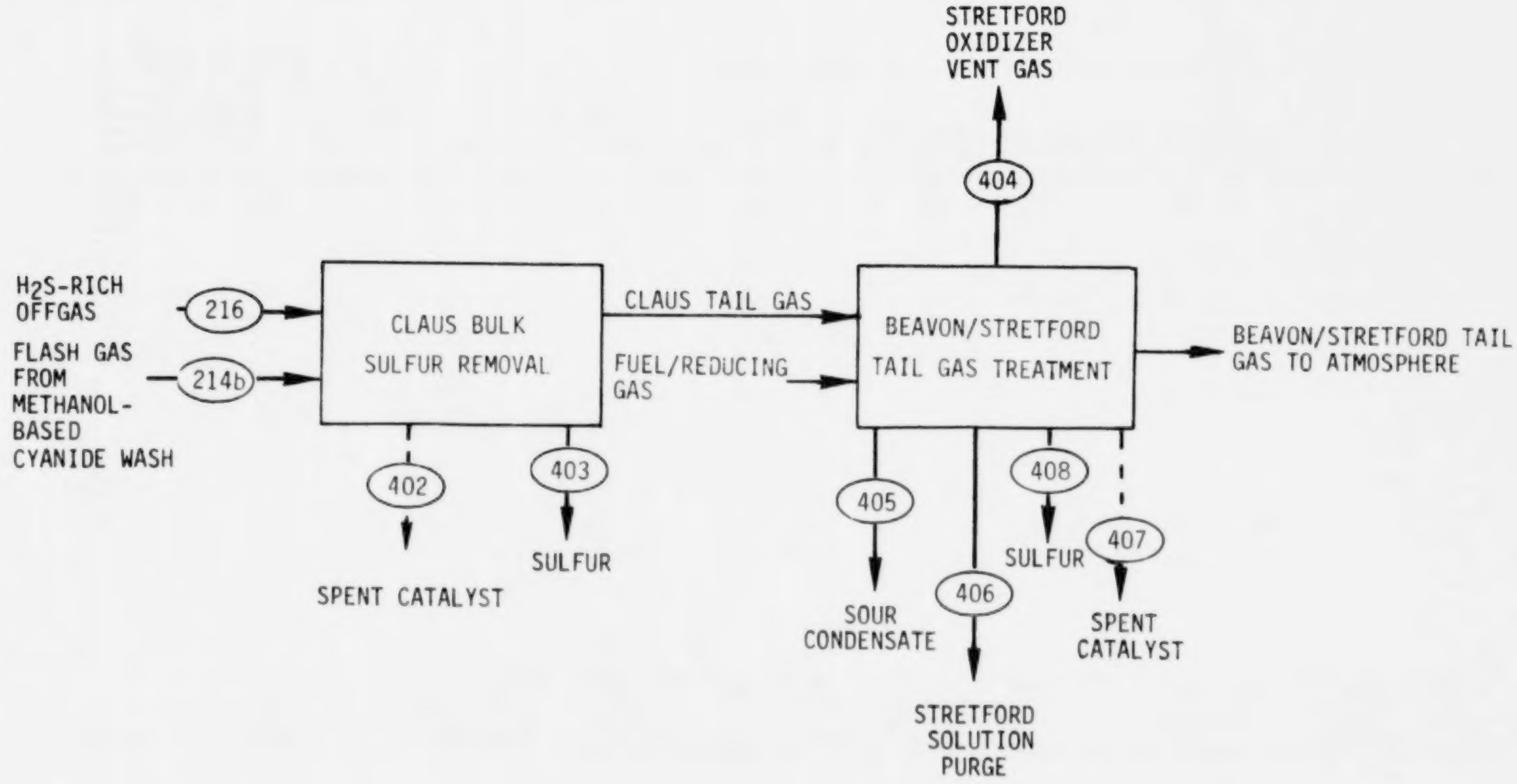
H$_2$S-RICH OFFGAS
216
FLASH GAS FROM METHANOL-BASED CYANIDE WASH
214b
CLAUS BULK SULFUR REMOVAL
402
SPENT CATALYST
403
SULFUR
CLAUS TAIL GAS
FUEL/REDUCING GAS
BEAVON/STRETFORD TAIL GAS TREATMENT
404
STRETFORD OXIDIZER VENT GAS
BEAVON/STRETFORD TAIL GAS TO ATMOSPHERE
405
SOUR CONDENSATE
406
STRETFORD SOLUTION PURGE
408
SULFUR
407
SPENT CATALYST

Figure 4-3. Example 1 - Claus bulk sulfur removal with Beavon/Stretford tail gas treatment

TABLE 4-6. EXAMPLE 1 - MATERIAL FLOW ESTIMATES FOR INTEGRATED CONTROL EMPLOYING CLAUS BULK SULFUR REMOVAL WITH BEAVON/STRETFORD TAIL GAS TREATMENT*

	Rectisol H_2S-Rich Offgas Stream 216		Cyanide Wash Flash Gas Methanol Wash Case Stream 214b		Combined Claus Feed Gas		Claus Tail Gas		Claus Sulfur Stream 403	Fuel Gas		Beavon/Stretford Tail Gas		Stretford Sulfur Stream 408	Sour Condensate Stream 405
	kmol/hr	Vol	kmol/hr	Vol	kmol/hr	Vol	kmol/hr	Vol	kg/hr	kmol/hr	Vol	kmol/hr	Vol	kg/hr	kg/hr
H_2			0.49	3.0	0.49	892ppmv	0.33	0.04		33	26.9				
CO			4.4	26.4	4.4	0.8	2.9	0.3		78	63.3				
CO_2	271	50.8	1.2	7.3	272	49.5	310	36.8		12	9.8	402	35.6		
H_2S	222	41.6	7.3	44.7	229	41.7	7.8	0.9				0.008†	7ppmv		
COS	25	4.7	0.56	3.4	26	4.7	1.2	0.1				0.075†	74ppmv		
CS_2	2	0.4			2	0.3	0.07	78ppmv							
SO_2	0.1	218ppmv			0.1	211ppmv	3.9	0.5							
HCN	0.3	636ppmv	2.1	12.9	2.4	0.44									
N_2	6	1.2			6	1.2	512	60.7				721	63.9		
Methanol	7	1.3	0.3	1.8	7	1.3	4.7	0.6				4.7	0.4		
Sulfur									7857					411	
Total Dry Gas	533		16		549		843			123		1128			
H_2O							227					47			4027
Total kmol/hr	533		16		549		1070			123		1175			
kg/hr	21544		524		22068		32926		7857	2784		38893		411	4027

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*The number of significant figures shown in some cases do not represent the degree of accuracy and are retained for material balance purposes only. Nevertheless, slight imbalances do appear as a result of numerical rounding. Material flow estimates are based upon published data and engineering estimates. Performance data and references are detailed in the Control Technology Appendices.

†Residual sulfur levels are based upon 100 ppmv total sulfur (Claus tail gas basis).

‡Some level of residual reducing gas would be present in the Beavon/Stretford effluent. Concentrations of CO in the effluent ranging from 250 to 670 ppmv have been reported.

Secondary waste streams from the control system are: (1) spent Claus catalyst (Stream 402), (2) sour condensate (Stream 405), (3) Stretford solution purge (Stream 406), (4) Stretford oxidizer vent gas (Stream 404), and (5) spent Beavon catalyst (Stream 407). The Claus unit would have a bauxite or alumina catalyst inventory of approximately 50 Mg. Assuming a catalyst life of 5 years, the average spent Claus catalyst generation rate would be 10 Mg/year. Sour condensate is expected to contain dissolved sulfide and traces of NH_3 and would be generated at a rate of about 4 m^3/hr. Stretford solution purge (Stream 406) for control of thiosulfate and thiocyanate buildup may be present as a waste stream containing vanadium and sodium salts as thiosulfate, sulfate, carbonate, and thiocyanate. The solution purge rate is approximately 0.1 to 0.2 Mg/hr. Purge solution may either be regenerated or discarded (refer to Section 4.1.1). Oxidizer vent gas would consist primarily of air, water vapor, and CO_2 but may contain traces of NH_3. Insufficient data are available for estimating the flow rate of oxidizer vent gas. The cobalt molybdate Beavon hydrogenation catalyst inventory is approximately 15 Mg. Assuming a catalyst service life of three years, the average spent catalyst generation rate would be 5 Mg/year. In addition, sulfur from the Claus and Beavon/Stretford processes (Streams 403 and 408) is generated at a combined rate of 8.3 Mg/hr and may require disposal, depending upon sulfur quality and market considerations.

Cost estimates for the Claus and Beavon/Stretford units are summarized in Table 4-7. Estimates are presented on two bases: (1) total capital investment and annualized costs and (2) total capital investment and annualized costs as percentages of the uncontrolled base plant costs for the methanol synthesis case. All costs are presented on a 1980 basis. The total capital investment was found to be similar for the Claus and Beavon/Stretford units. However, annualized Claus costs were estimated to be about 70% lower than those for the Beavon/Stretford, primarily as a result of large credits associated with steam generated during Claus processing, and fuel gas require-

TABLE 4-7. EXAMPLE 1 - COSTS OF INTEGRATED CLAUS BULK SULFUR REMOVAL WITH BEAVON/STRETFORD TAIL GAS TREATMENT (1980 BASIS)

	Total Capital Investment		Annualized Cost	
	10^6 Dollars	% of Base Plant*	10^6 Dollars	% of Base Plant*
Claus Unit	8.7		0.41	
Beavon/ Stretford Unit	7.4		1.4	
Total	16.1	1.45	1.8	0.52

*Expressed as a percentage of the cost for an uncontrolled methanol synthesis facility.

ments for the Beavon/Stretford process. Capital and annualized costs for the integrated control system represent approximately 1.4% and 0.5% of the respective costs for the uncontrolled methanol synthesis base plant.

Performance and cost of the Claus/Beavon/Stretford control system are dependent upon both the feed gas flow rate and sulfur content. For example, if the selectivity of the Rectisol unit were reduced to produce a Claus feed gas of 15% total sulfur for the same coal sulfur content, the Claus feed gas flow rate would increase by a factor of about three and the Beavon/Stretford tail gas flow rate would increase by a factor of about two. Therefore, emissions from the Beavon/Stretford would also increase by a factor of about two. The resulting increases in capital costs for Claus and Beavon/Stretford units are estimated to be about 40% and 60%, respectively. Alternatively, with the same Rectisol selectivity (i.e., 47% sulfur in the Claus feed) for a coal having one-half the total sulfur content initially considered, the Claus feed gas rate and the Beavon/Stretford tail gas flow rate would decrease by about one-half. Therefore, emissions from the Beavon/Stretford would also decrease by about one-half. The resulting decreases in capital costs for Claus and Beavon/Stretford units are estimated to be about 40% and 35%, respectively.

Example 2 - Claus Bulk Sulfur Removal with SCOT Tail Gas Treatment and Incineration

This example illustrates treatment of the combined H_2S-rich Rectisol acid gas (Stream 216) and the flash gas from a methanol-based cyanide wash unit (Stream 214b) in a Claus bulk sulfur removal unit with SCOT tail gas treatment and thermal incineration. The control system is presented schematically in Figure 4-4, and material flow estimates are presented in Table 4-8. Assumptions relating to Claus unit performance are idential to those presented for Example 1 although in this example the SCOT recycle gas represents an additional Claus feed gas stream.

The SCOT unit is reported to be capable of reducing Claus tail gas residual sulfur concentrations to about 250 ppmv (dry Claus tail gas basis). A CO-rich fuel gas has been used in this example to reheat the Claus tail gas, catalytic reduction of SO_2, and subsequent incineration. The resulting sulfur emission rate is about 0.2 kmol/hr SO_2 from tail gas treatment and incineration. While methanol present in the Claus tail gas is not expected to be affected by SCOT tail gas treatment, essentially complete destruction would be achieved during incineration.

Secondary waste streams from the control system are: (1) spent Claus catalyst (Stream 402), (2) sour condensate (Stream 409), and (3) spent SCOT catalyst (Stream 410). As in Example 1, spent Claus catalyst would be generated at an average rate of approximately 10 Mg/yr assuming a 5 year catalyst life. The sour condensate is expected to contain dissolved sulfide and traces of NH_3 and would be generated at a rate of 4 m^3/hr. The cobalt molybdate SCOT hydrogenation catalyst inventory is approximately 15 Mg. Assuming a catalyst

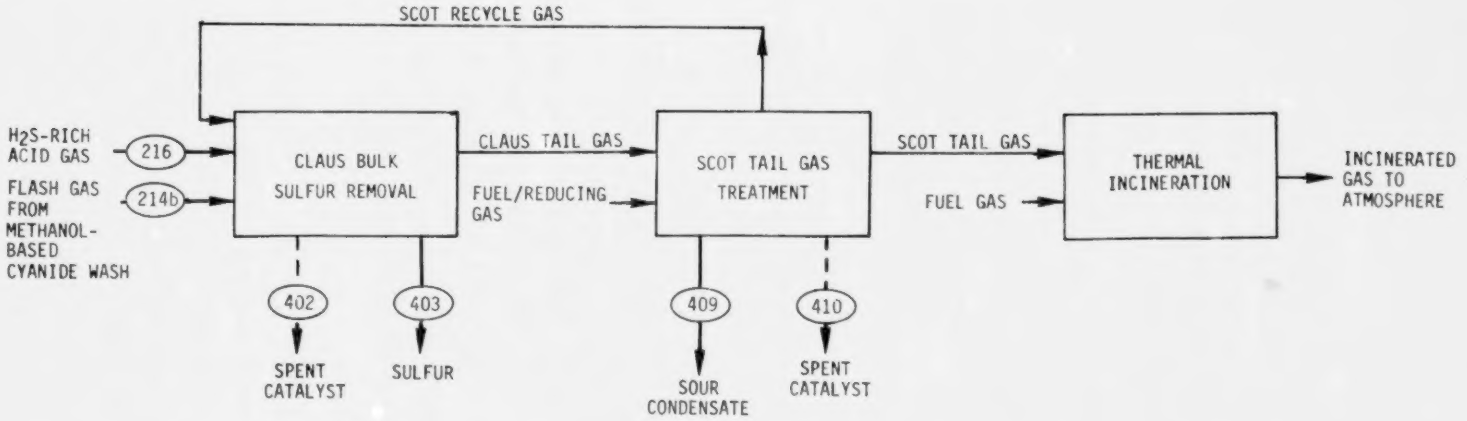

Figure 4-4. Example 2 - Claus bulk sulfur removal with SCOT tail gas treatment and incineration

TABLE 4-8. EXAMPLE 2 - MATERIAL FLOW ESTIMATES FOR INTEGRATED CONTROL EMPLOYING CLAUS BULK SULFUR REMOVAL, SCOT TAIL GAS TREATMENT, AND INCINERATION*

	H_2S-Rich Offgas Stream 216		Cyanide Wash Flash Gas Methanol Wash Case Stream 214b		SCOT Recycle Gas		Combined Claus Feed Gas		Claus Tail Gas		Claus Sulfur Stream 403	SCOT Fuel Gas		SCOT Tail Gas		Sour Condensate Stream 409	Incineration Fuel Gas		Incineration Tail Gas	
	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kg/hr	kmol/hr	Vol %	kmol/hr	Vol %	kg/hr	kmol/hr	Vol %	kmol/hr	Vol %
H_2			0.49	3.0	0.28	0.6	0.8	0.1	0.46	500ppmv		38	26.9				40	26.9		
CO			4.4	26.4	2.4	5.0	6.8	1.1	4.1	0.5		89	63.3				94	63.1		
CO_2	271	50.8	1.2	7.3	32	66.8	304	50.9	340	37.7		14	9.8	411	34.5		15	9.8	520	33.6
H_2S	222	41.6	7.3	44.7	13	27.6	242	40.5	8.1	0.9				0.2[†]	168ppmv					
COS	25	4.7	0.56	3.4			26	4.4	1.2	0.1				0.04[†]	34ppmv					
CS_2	2	0.4					2	0.3	0.07	78ppmv										
SO_2	0.1	218ppmv					0.1	168ppmv	4.1	0.5									0.2	129ppmv
HCN	0.3	636ppmv	2.1	12.9			2.4	0.4												
N_2	6	1.2					6	1.0	538	59.7				776	65.1				1029	66.4
Methanol	7	1.3	0.3	1.8			7	1.2	4.7	0.5				4.7	0.4					
Sulfur											8260									
Total Dry Gas	533		16		48		597		901			141		1192			149		1549	
H_2O					2		2		242					50		3978			90	
Total kmol/hr kg/hr	 533 21544		 16 524		 50 1984		 599 24052		 1220 35295		 8260	 141 2569		 1244 40889		 3978	 149 2715		 1639 5335	

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*The number of significant figures shown in some cases do not represent the degree of accuracy and are retained for material balance purposes only. Nonetheless slight imbalances do appear as a result of numerical rounding. Material flow estimates are based upon published data and engineering estimates. Performance data and references are detailed in the Control Technology Appendices.

[†] Residual sulfur levels are based upon 250 ppmv total sulfur (Claus plant tail gas basis).

life of 5 years, the average spent catalyst generation rate would be 3 Mg/yr. In addition, Claus sulfur is produced at a rate of about 8.3 Mg/hr and may require disposal, depending upon sulfur quality and market considerations.

Cost estimates for the Claus, SCOT, and incineration units are summarized in Table 4-9. Estimates are presented on two bases: (1) total capital investment and annualized cost, and (2) total capital investment and annualized cost percentages of the uncontrolled base plant cost for the methanol synthesis case. All costs are presented on a 1980 basis. The total capital investment for the combined SCOT/incineration system was estimated to be nearly 30% lower than the capital investment for the Claus unit. However, annualized Claus costs are estimated to be about 80% lower than those for the combined SCOT/incineration system. This is primarily due to large credits associated with steam generated during Claus processing, and fuel gas requirements for tail gas treatment and incineration. Capital and annualized costs for the integrated control system represent approximately 1.4% and 0.7% of the respective costs for the uncontrolled methanol synthesis base plant.

The effects of feed gas flow rate and sulfur content upon the control system's performance and cost have been discussed in Example 1. Similar conclusions can be drawn with respect to the effects of these parameters upon the Claus/SCOT/incineration control system.

Example 3 - Claus Bulk Sulfur Removal with Wellman-Lord Tail Gas Treatment

This example illustrates treatment of the combined H_2S-rich Rectisol acid gas (Stream 216) and the flash gas from a methanol-based cyanide wash unit (Stream 214b) in a Claus bulk sulfur removal unit with Wellman-Lord tail gas treatment. The control system is presented schematically in Figure 4-5, and material flow estimates are presented in Table 4-10. Assumptions relating to Claus unit performance are identical to those presented in Example 1, although in this example the Wellman-Lord recycle gas represents an additional Claus feed stream.

TABLE 4-9. EXAMPLE 2 - COSTS OF INTEGRATED CLAUS BULK SULFUR REMOVAL WITH SCOT TAIL GAS TREATMENT AND INCINERATION (1980 BASIS)

	Total Capital Investment		Annualized Cost	
	10^6 Dollars	% of Base Plant*	10^6 Dollars	% of Base Plant*
Claus Unit	9.2		0.44	
SCOT Unit	6.3		1.9	
Incineration Unit	0.42		0.63	
Total	15.9	1.44	3.0	0.86

*Expressed as a percentage of the cost for an uncontrolled methanol synthesis facility.

The Wellman-Lord unit is reported to be capable of reducing Claus tail gas residual sulfur concentrations to about 250 ppmv (dry Claus tail gas basis). In this example, the corresponding Wellman-Lord tail gas sulfur concentration is about 150 ppmv. A methane-rich fuel gas has been used for Claus tail gas incineration in this example consistent with the design upon which the Wellman-Lord flow estimates are based. In an integrated facility other fuels may be preferable. The resulting sulfur emission rate is about 0.2 kmol/hr SO_2 in the Wellman-Lord tail gas. Minor constituents such as methanol, CO and NH_3 which may be present in the Claus tail gas are expected to be effectively destroyed during the incineration step of tail gas treatment.

Secondary waste streams from the control system are: (1) spent Claus catalyst (Stream 402), (2) sour condensate (Stream 411), and (3) thiosulfate/

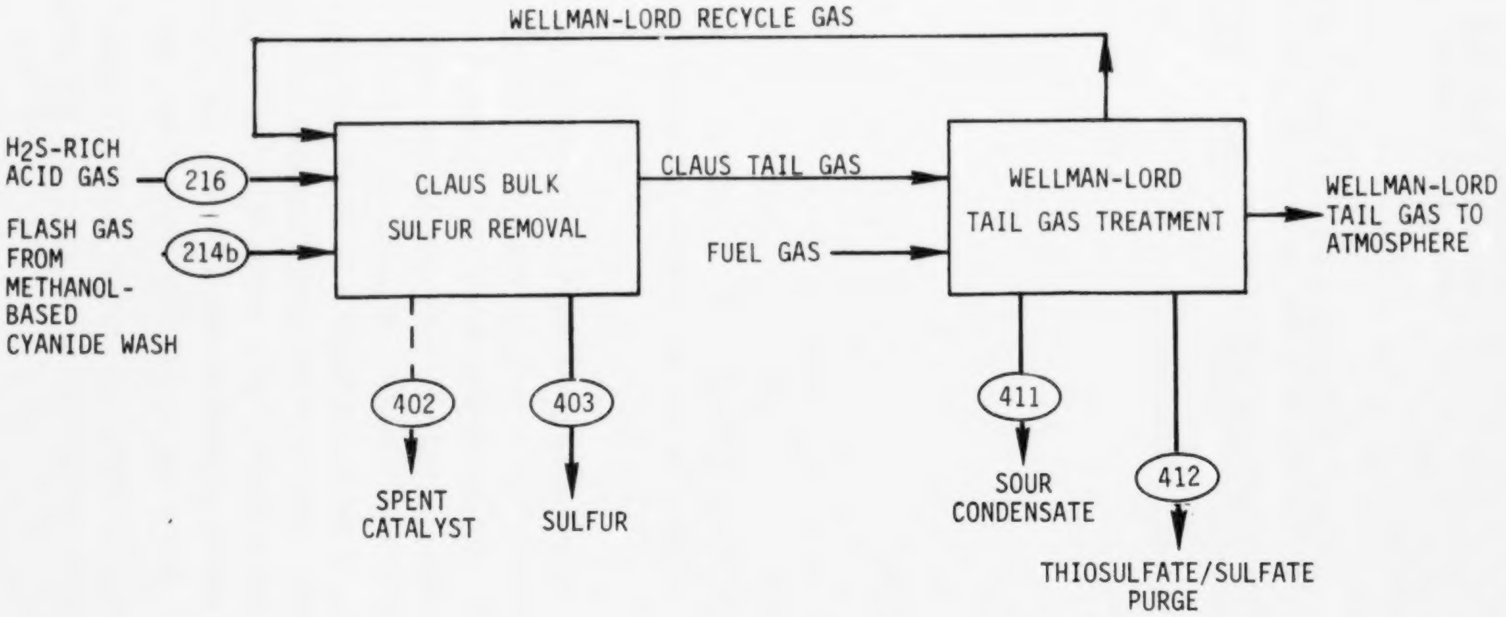
WELLMAN-LORD RECYCLE GAS
H_2S-RICH ACID GAS
216
FLASH GAS FROM METHANOL-BASED CYANIDE WASH
214b
CLAUS BULK SULFUR REMOVAL
CLAUS TAIL GAS
FUEL GAS
WELLMAN-LORD TAIL GAS TREATMENT
WELLMAN-LORD TAIL GAS TO ATMOSPHERE
402
SPENT CATALYST
403
SULFUR
411
SOUR CONDENSATE
412
THIOSULFATE/SULFATE PURGE

Figure 4-5. Example 3 - Claus bulk sulfur removal with Wellman-Lord tail gas treatment

TABLE 4-10. EXAMPLE 3 - MATERIAL FLOW ESTIMATES FOR INTEGRATED CONTROL EMPLOYING CLAUS BULK SULFUR REMOVAL WITH WELLMAN-LORD TAIL GAS TREATMENT*

	H_2S-Rich Offgas Stream 216		Cyanide Wash Flash Gas Methanol Wash Case Stream 214b		Wellman-Lord Recycle Gas		Combined Claus Feed Gas		Claus Tail Gas		Claus Sulfur Stream 403	Fuel Gas[†]		Wellman-Lord Feed Gas		Sour Condensate Stream 411	Wellman-Lord Tail Gas	
	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kmol/hr	Vol %	kg/hr	kmol/hr	Vol %	kmol/hr	Vol %	kg/hr	kmol/hr	Vol %
H_2			0.49	3.0			0.49	0.09	0.34	0.04								
CO			4.4	26.4			4.4	0.8	3.1	0.4								
CO_2	271	50.8	1.2	7.3			272	48.4	302	38.5				352	27.0		352	27.2
H_2S	222	41.6	2.3	44.7			229	40.7	8.1	1.0								
COS	25	4.7	0.56	3.4			26	4.6	1.2	0.2								
CS_2	2	0.4					2	0.4	0.07	87ppmv								
SO_2	0.1	218ppmv			13	100	13	2.3	4.1	0.5				14	1.0		0.2[‡]	147ppmv
HCN	0.3	636ppmv	2.1	12.9			2.4	0.4										
N_2	6	1.2					6	1.1	461	58.7				920	70.4		920	71.2
O_2														20	1.5		20	1.5
CH_4												35	94					
C_2H_6												2.2	6					
Methanol	7	1.3	0.3	1.8			7	1.2	5.2	0.7								
Sulfur																		
Total Dry Gas	533		16		13		562		785		8260	37		1306			1292	
H_2O					7		7		232					327		3297	143	
Total																		
kmol/hr	533		16		19		569		1017			37		1682			1435	
kg/hr	21544		524		938		23006		31270		8260	623		48651		3297	44484	

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[*] The number of significant figures shown in some cases do not represent the degree of accuracy and are retained for material balance purposes only. Nonetheless, slight imbalances do appear as result of numerical rounding. Material flow estimates are based upon published data and engineering estimates. Performance data and references are detailed in the Control Technology Appendices.

[†] A methane-rich fuel gas has been used in this example consistent with the design upon which the Wellman-Lord flow estimates are based. In an integrated facility other fuel gases may be preferable.

[‡] The SO_2 emission rate is based upon 250 ppmv total sulfur (Claus plant tail gas basis).

sulfate by-product purge (Stream 412). As in Example 1, spent Claus catalyst would be generated at an average rate of approximately 10 Mg/yr, assuming a 5-year catalyst life. The sour condensate typically has a pH value between 1 and 2 and would be generated at a rate of 3 m^3/hr. By-product purge consists primarily of sodium salts such as sulfite, pyrosulfite, sulfate, and thiosulfate with approximately 29% water. By-product purge is generated at a rate of 90 kg/hr. In addition, Claus sulfur is produced at a rate of about 8.3 Mg/hr and may require disposal, depending upon sulfur quality and market considerations.

Cost estimates for the Claus and Wellman-Lord units are summarized in Table 4-11. Estimates are presented on two bases: (1) total capital investment and annualized costs, and (2) total capital investment and annualized cost as percentages of the uncontrolled base plant cost for the methanol synthesis case. All costs are presented on a 1980 basis. The total capital investment was found to be similar for the Claus and Wellman-Lord units. However, annualized Claus costs are estimated to be about 90% lower than those for the Wellman-Lord unit. This is primarily due to large credits associated with steam generated during Claus processing, and fuel gas requirements for tail gas incineration. Capital and annualized costs for the integrated control system represent approximately 1.8% and 1.2% of the respective costs for the uncontrolled methanol synthesis base plant.

The effects of feed gas flow rate and sulfur content upon the control system's performance and cost have been discussed in Example 1. Similar conclusions can be drawn with respect to the effects of these parameters upon the Claus/Wellman-Lord control system.

TABLE 4-11. EXAMPLE 3 - COSTS OF INTEGRATED CLAUS BULK SULFUR REMOVAL WITH WELLMAN-LORD TAIL GAS TREATMENT (1980 BASIS)

	Total Capital Investment		Annualized Cost	
	10^6 Dollars	% of Base Plant*	10^6 Dollars	% of Base Plant*
Claus Unit	9.2		0.44	
Wellman-Lord Unit	11		3.7	
Total	20	1.8	4.1	1.2

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*Expressed as a percentage of the cost for an uncontrolled methanol synthesis facility.

4.1.2 Combustion Gases

Combustion of many types of fossil fuels produces a gas stream that contains undesirable amounts of SO_2, NO_x, and/or particulates. Sulfur dioxide is formed rapidly in the combustion process when sulfur contained in the fuel reacts with oxygen in the air. Variations in the combustion process are not effective in reducing SO_2 emissions. Rather, sulfur must be removed from the fuel or, once formed, SO_2 must be removed from the exhaust gas.

The generation of NO_x from air-fed fuel combustion processes occurs by two separate mechanisms, namely thermal NO_x formation and fuel NO_x formation. Thermal NO_x results from the thermal fixation of molecular nitrogen and oxygen in the combustion air and is sensitive to flame temperatures and to local concentrations of oxygen. Fuel NO_x is created from the oxidation of chemically-bound nitrogen in the fuel being combusted. Fuel NO_x formation is strongly affected by the rate of mixing of the fuel and air and by the local oxygen concentration. Approximately 95% of nitrogen oxides from combustion are emitted as NO (83,84).

The particulates generated during combustion result mainly from the ash content of the fuel. The magnitude of these emissions in the flue gas is a function of combustion unit design and ash content of the fuel. Particulate emissions are very low when oil-based fuels are used and are negligible with gaseous fuels.

Combustion gases will also contain CO and very small amounts of unburned organics (including polycyclic compounds). Concentrations of these components are a function of both the fuel burned and the design and operation of the combustion unit. Trace elements present in the fuel may also be present in flue gases. Ordinarily, however, no controls are applied to combustion gases specifically for control of CO, organics, or trace elements. Some degree of trace elements control is achieved as part of particulate removal.

Section 4
Combustion Gases

The major sources of flue gases from a K-T based indirect liquefaction facility are the power boiler, process heaters, gas turbines, and secondary combustion gas streams from other media. In this section control technologies applicable to the removal of nitrogen oxides, particulates, and sulfur oxides from such stationary sources are discussed.

NO_x Control

NO_x pollution control techniques are of two types: (1) those that limit nitrogen conversion to NO_x by modifying combustion characteristics and (2) flue gas treatment techniques (i.e., removal of NO_x after it is formed).

Combustion modification techniques are the most widely used techniques. They can achieve from 25 to 60% reduction in NO_x emissions. Some of the common combustion modification techniques are (1) low excess air, (2) staged combustion, (3) flue gas recirculation, (4) reduced load, (5) low NO_x burners, and (6) ammonia injection. The key features and unit costs of these techniques are discussed in Table 4-12.

Low excess air level in the furnace has generally been found to be an effective method for NO_x control. In this technique, the combustion air is reduced to the minimum amount required for complete combustion while maintaining acceptable furnace cleanliness and steam temperature. With less oxygen available in the flame zone, both thermal and fuel NO_x formation are reduced. In addition, the reduced air flow lowers the quantity of flue gas released resulting in an improvement in boiler efficiency.

Staged combustion produces overall fuel-rich conditions during the first couple of seconds and promotes the reduction of NO to N_2. Various methods to achieve this are available. Overfire Air and Burners Out of Service are two techniques generally used on coal fired boilers. Details regarding their performance and applicability are provided in Table 4-12.

Flue gas recirculation (FGR) consists of recycling a portion of the flue gas back to the primary combustion zone. This reduces NO formation by lowering the bulk gas temperature and oxygen concentration. This technique, however, is effective only on oil and gas fired boilers.

Load reduction can be used to decrease NO_x emissions. Thermal NO_x formation generally increases as the volumetric heat release rate or combustion

TABLE 4-12. COMBUSTION MODIFICATION TECHNIQUES FOR NO_x CONTROL

Control Technique	Description of Technique	Efficiency (as % NO_x Reduction)	Type of Fuel Fired	Range of Application
Low Excess Air (LEA)	Combustion air is reduced to the minimum amount required for complete combustion while maintaining proper stream temperature.	0 - 25	Pulverized coal	Excess O_2 lowered to 5.2% on the average.
		5 - 25	Stoker coal	Excess O_2 limited to 5-6% minimum.
		0 - 28 0 - 24	Residual oil Distillate oil	Excess O_2 can be reduced to <3%.
		5 - 35	Natural gas	Excess O_2 can be reduced to <3%.
Staged Combustion				
Overfire Air Injection (OFA)	Injection of air above the top burner level through OFA ports together with a reduction in air flow to the burners (staged combustion).	5 - 30	Pulverized coal	Burner O_2 can be as low as stoichiometric
Staged Combustion Air (LEA + OFA)	Reduction of under grate air flow and increase of overfire air flow.	5 - 25	Stoker coal	Excess O_2 limited to 5% minimum.
	Fuel rich firing burners with secondary combustion air ports.	20 - 50 17 - 44	Residual oil Distillate oil	70-90% burner stoichiometry can be used with proper burner installation.
	Injection of secondary air downstream of the burner(s) in the direction of the flue gas path.	5 - 46	Natural gas	70-90% burner stoichiometries can be maintained. Applicable to all units, however, requires extensive equipment modification.

(Continued)

TABLE 4-12. (CONTINUED)

Control Technique	Type of Fuel Fired	Stage of Development	Secondary Waste	Cost	Limitations and Comments
Low Excess Air (LEA)	Pulverized Coal	Available but implemented on a limited basis only.	None	Capital: \$440 to \$550/MW heat input Operating: 0 to 8 mills/10^3 kg steam	Limited by increase in CO, HC, and particulate emissions. Increase in boiler efficiency may be achieved as a benefit.
	Stoker coal	Available now but need R&D on lower limit of air.	None	Capital: \$600 to \$1850/MW heat input Operating: 13 to 57 mills/10^3 kg steam	Danger of overheating grate, clinker formation, corrosion, and high CO emissions.
	Residual Oil Distillate Oil	Available.	None	Capital: \$460 to \$2400/MW of heat input Operating: <83 mills/10^3 kg steam	Added benefits include increase in boiler efficiency. Limited by increase in CO, HC, and TSP emissions.
	Natural Gas	Available.	None	Capital: \$580/MW of heat input Operating: --	Generally practical because of increase in boiler efficiency. Best NO_x reductions reported for large multi-burner units.
Staged Combustion					
Overfire Air Injection (OFA)	Pulverized Coal	Available but not demonstrated.	None	Capital: \$800 to \$940/MW heat input Operating: 80 to 85 mills/10^3 kg steam	Limited by possible increase in slagging and corrosion. Excess air may be required to ensure complete combustion thereby decreasing efficiency.
Staged Combustion Air (LEA + OFA)	Stoker Coal	Most stokers have OFA ports as smoke control but may need better air flow control devices.	None	Capital: \$600 to \$800/MW heat input Operating: 24 to 32 mills/10^3 kg steam	Overheating grate, corrosion, and high CO emissions can occur if under grate air flow is reduced below acceptable level as in LEA.
	Residual Oil Distillate Oil	Technique is applicable on packaged and field-erected units. However, not commercially available for all design types.	None	Capital: \$870 to \$5150/MW of heat input Operating: 123 to 370 mills/10^3 kg steam	Best implemented on new units. Retrofit is probably not feasible for most units especially packaged ones.
	Natural Gas	Technique is still experimental especially for small firetube and watertube units.	None	Capital: \$1070/MW of heat input Operating: 117 mills/10^3 kg steam	Found to be less effective on firetube boilers than watertube boilers. Generally less effective for gas-fired units.

(Continued)

TABLE 4-12. (CONTINUED)

Control Technique	Description of Technique	Efficiency (as % NO_x Reduction)	Type of Fuel Fired	Range of Application
Staged Combustion				
Air and Fuel Rich Firing	One or more burners fired on air only. Remainder of burners firing fuel rich.	27 - 39	Pulverized coal	Boilers must have a minimum of 4 burners, or designed with excess burners.
Flue Gas Recirculation (FGR)	Recirculation of the flue gas to the burner windbox.	0 - 20	Pulverized coal	A maximum of 25% of the flue gas can be recirculated.
		15 - 30	Residual oil	Up to 25-30% of flue gas recycled. Can be implemented on all design types.
		58 - 73	Distillate oil	
		48 - 86	Natural gas	Flue gas recirculation rates possible up to 45%. Technique is applicable to all boiler types except ones equipped with ring burners.
Reduced Load	Reduction of fuel and air flow to the burner.	Up to 45%	Pulverized coal	Load may be reduced to 25% of capacity.
		Average 15%	Stoker coal	Load may be reduced to 25%.

(Continued)

TABLE 4-12. (CONTINUED)

Control Technique	Type of Fuel Fired	Stage of Development	Secondary Waste	Costs	Limitations and Comments
Staged Combustion					
Air and Fuel Rich Firing	Pulverized Coal	Available, but engineering refinement is needed prior to implementation.	None	Not available	Load reduction required in most cases. Possible increased slagging and corrosion. New boiler design will incorporate the required number of burners.
Flue Gas Recirculation	Pulverized Coal	Not offered because the method is comparatively ineffective.	None	Not available	Flue gas recirculation lowers the bulk furnace gas temperatures and reduces O_2 concentration in the combustion zone. Requires installation of flue gas recirculation ducts, fans, insulation, etc. May cause combustion instability.
	Residual Oil Distillate Oil	Available. Requires extensive modifications to the burner and windbox.	None	Capital: $1070 to $5150/MW of heat input Operating: 196 to 438 mills/10^3 kg of steam	Best suited for new units. Costly to retrofit. Possible flame instability at high FGR rates.
	Natural Gas	Available now. Best suited for new boilers. Retrofit application would result in extensive burner modifications.	None	Capital: $870 to $1070/MW of heat input	Flame instability problem is not severe except for ring burners. Minor burner modifications can guarantee stable flames. Most effective on watertube units.
Reduced Load	Pulverized Coal	Available but not implemented because of negative operational impacts.	None	Not available	Best used with increase in firebox size for new boilers. Load reduction may not be effective because of increase in excess O_2.
	Stoker Coal	Available.	None	Not available	Only for stokers that can reduce load without increasing excess air. Not a desirable technique because of loss in boiler efficiency.

(Continued)

TABLE 4-12. (CONTINUED)

Control Technique	Description of Technique	Efficiency (as % NO_x Reduction)	Type of Fuel Fired	Range of Application
Reduced Load		33% decrease to 25% increase*	Residual oil	Applicable to all boiler types and sizes. Load can be reduced to 25% of maximum.
		31% decrease to 17% increase*	Distillate oil	
		32% decrease to 82% increase*	Natural gas	Tests to 20% of rated capacity. Applicable to all units.
Low NO_x Burners	New burner designed to utilize controlled air-fuel mixture.	45 - 60	Pulverized coal	Prototypes are limited to size ranges >30 MW.
		20 - 50 20 - 50	Residual oil Distillate oil all boilers.	New burners described generally applicable to all boilers.
		20 - 50	Natural gas	More specific information needed.
NH_3 Injection	Injection of NH_3 into convective section of the boiler.	40 - 60	Pulverized coal	NH_3 injection rate limited to $\frac{NH_3}{NO} = 1.5$
		40 - 70 40 - 70	Residual oil Distillate oil	Applicable for large package and field-erected watertube boilers.
		40 - 70	Natural gas	Not feasible for firetube boilers.

(Continued)

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*Apparent increases in NO_x are indicated by limited test data and need confirmation. Such increases could be due to higher oxygen levels at reduced loads relative to oxygen levels at design load.

TABLE 4-12. (CONTINUED)

Control Technique	Type of Fuel Fired	Stage of Development	Secondary Waste	Costs	Limitations and Comments
Reduced Load	Residual Oil Distillate Oil	Available now as a retrofit application. Better implementation with improved firebox design.	None	Not Available	Technique not effective when it necessitates an increase in excess O_2 levels, RL is possible to implement in new designs as reduced combustion intensity (enlarged furnace plan area).
	Natural Gas	Technique available. However, retrofit application is not feasible due to initial low load factor of industrial units.	None	Not Available	Least effective on firetube boilers because of lower combustion intensity. Applicable for new watertube units with increased firebox size.
Low NO_x Burners	Pulverized Coal	Development stage prototypes are available from major boiler manufacturers.	None	Capital: $800 to $940/MW of heat input Operating: 80 to 85 mills/10^3 kg steam	Low NO_x burners could maintain the furnace in an oxidizing environment to minimize slagging and reduce the potential for furnace corrosion. More complete carbon utilization results because of better coal/air mixing in the furnace. Lower O_2 requirements may be obtained with all the combustion air admitted through the burners.
	Residual Oil Distillate Oil	Commercially offered but not demonstrated.	None	Capital: $860 to $5150/MW of heat input Operating: 123 to 376 mills/10^3 kg steam	Specific emissions data from oil fired industrial boilers equipped with LNB are lacking.
	Natural Gas	Commercially offered but not demonstrated.	None	Capital: $860 to $1070/MW of heat input Operating: 106 to 117 mills/10^3 kg steam	Specific emissions data from gas fired industrial boilers equipped with LNB are lacking.
NH_3 Injection	Pulverized Coal	Commercially offered but not demonstrated.	Ammonium Bisulfate	Capital: $4800/MW of heat input Operating: 247 mills/10^3 kg steam	Limited by furnace geometry. Performance is sensitive to flue gas temperature and residence time at optimum temperatures. By-product emissions such as ammonium bisulfate could cause operational problems.
	Residual Oil Distillate Oil	Commercially offered but not demonstrated.	Ammonium Bisulfate	Capital: $4940 to $9770/MW of heat input Operating: 266 to 433 mills/10^3 kg of steam Not available for natural gas	Some increased maintenance of air heater/economizer parts might be necessary when burning high sulfur oil. Technique is very costly. Should have fewer problems when firing natural gas.
	Natural Gas	Not available.	---	---	---

intensity increases. Reduced combustion intensity can be brought about by load reduction by either derating the boiler or using an enlarged firebox.

Low NO_x burners have been developed primarily for reducing NO_x emissions from utility boilers. Their principal characteristics are reduced flame turbulance, delayed fuel air mixing, and establishment of fuel-rich zones where combustion initially takes place. It is now standard practice for all utility boilers to come equipped with low NO_x burners.

The process of injecting ammonia was developed by Exxon Research and Engineering Company. This technique acts by reducing NO to elemental nitrogen and oxygen with NH_3 at flue gas temperatures ranging from approximately 1070 to 1290K. However, optimal NO reduction occurs over a very narrow temperature range, around 1240K ±50K.

The cost of combustion modification techniques for controlling NO_x emissions depends upon (1) the additional hardware required and (2) any changes in operational procedures that may increase the cost of steam production. Cost estimates for combustion modification techniques are provided in Table 4-12. For more detailed information other EPA studies should be consulted (83,84).

Flue gas treatment techniques have been proposed for control of NO_x emissions to levels significantly below those achievable by combustion modification techniques. Although large scale flue gas treatment schemes have not been proved commercially in the U.S., these techniques are being applied in Japan. The key features of some of these processes are provided in Table 4-13.

Of the processes listed in Table 4-13, the Selective Catalytic Reduction (SCR) system, using ammonia to react with NO_x, is perhaps the most promising. SCR commercial units are being applied on many gas and oil-fired boilers in Japan. Full scale tests of coal-fired boilers are scheduled in mid-1982; two units are operating and several more are due online. Considerable

TABLE 4-13. NO_x FLUE GAS TREATMENT CONTROL ALTERNATIVES FOR BOILERS*

Control Technique	Description of Technique	Principle of Operation	Efficiency (% as NO_x Reduction)	Applicability
Selective Catalytic Reduction (SCR) - Fixed Packed Bed Reactors	Utilizes NH_3 to selectively reduce NO_x to N_2.	Reactor contains ring shaped catalyst pellets packed in fixed bed.	Up to 90%	Applicable only to flue gas streams containing particulate emissions of less than 20 mg/Nm^3.
- Moving Bed Reactors	Utilizes NH_3 to selectively reduce NO_x to N_2.	Reactor contains catalyst (rings or pellets) gravity-fed mechanically-screened, and returned to reactor.	Up to 90%	Applicable only to flue gas streams containing particulates at less than 1 g/Nm^3.
- Parallel Flow Reactor	Utilizes NH_3 to selectively reduce NO_x to N_2.	Reactor contains a special catalyst arrangement (honeycomb, parallel plate, or tubes).	Up to 90%	Testing currently under way for high particulate (>1 g/Nm^3) flue gas.
Absorption-Oxidation	Removes NO_x from flue gas by absorbing the NO or NO_x into a solution containing an oxidant which converts the NO_x to a nitrate salt.	Use of gas/liquid contactors. Perforated plate and packed towers accomplish NO_x absorption by generating high gas/liquid ratio.	The relative insolubility of NO in water will prohibit a high efficiency.	No published information available.
SCR - NO_x/SO_x Removal	Utilizes NH_3 to catalytically reduce NO_x after SO_x is absorbed and reacted with catalyst.	Reactor and catalyst removes both NO_x and SO_2, uniquely designed parallel flow reactor used to avoid particulate problems.	80% NO_x reduction, 90% SO_x reduction (theoretical).	Should be applicable to high particulate flue gas.

(Continued)

TABLE 4-13. (CONTINUED)

Control Technique	Stage of Development	Secondary Wastes	Costs	Limitations and Comments
SCR - Fixed Packed Bed Reactors	Commercially available only for natural gas-fired boilers at this time.	Spent catalyst	20MW estimate: Capital: $155/kW (coal) $84/kW (oil) $32/kW (gas) Operating: 2.5 mills/kWh (coal) 2.3 mills/kWh (oil) 1.4 mills/kWh (gas)	Although it is possible to install a hot ESP to reduce the particulate level to 20 mg/Nm^3, this is expensive and not always effective. Thus, fixed bed SCR systems are not considered for application to coal-fired boilers.
SCR - Moving Bed Reactors	Has been applied in Japan to several oil-fired industrial and utility boilers.	Spent catalyst	20MW estimate: Capital: $110/kW (coal) $84/kW (oil) Operating: 2.4 mills/kWh (coal) 2.5 mills/kWh (oil)	Although it is possible to install a hot ESP to reduce the particulate level to 1 g/Nm^3, this is expensive and not always effective. Thus, moving bed SCR systems are not considered for application to coal-fired boilers.
SCR - Parallel Flow Reactor	Had been applied in Japan to several oil-fired industrial and utility boilers. Applicability to coal-fired boilers currently being tested by EPA.	Spent catalyst	20MW estimate: Capital: $53/kW (coal) $46/kW (oil) Operating: 1.8 mills/kWh (coal)	Greatly reduces particulate impaction as gas flow is parallel to catalyst surface. Unreacted NH_3 downstream can react with SO_2 or SO_3 to form ammonium bisulfate or the NH_3 could enter FGD and ESP equipment.
Absorption-Oxidation	No coal-fired tests have been made.	NO_3^- salts in wastewater	20MW estimate Capital: $597/kW (coal Operating: 9.6 mills/kWh (coal)	The presence of particulates requires a prescrubber. The presence of SO_2 requires FGD pretreatment. Increased NO_x concentration requires a larger column height and increased oxidant concentration. Nitrate salts formed as a secondary pollutant.
SCR - NO_x/SO_x Removal	No continuous coal-fired NO_x removal test data for NO_x/SO_x systems are available.	Spent catalyst	20MW estimates Capital: $567/kW (coal & oil) Operating: 6 mills/kWh (coal & oil)	System is not affected by changes in the boiler gas flow rate or particulate concentrations. Changes in NO_x concentration because of boiler load changes may be compensated for by conventional control system used with the NH_3 injection equipment.

(Continued)

TABLE 4-13. (CONTINUED)

Control Technique	Description of Technique	Principle of Operation	Efficiency (% as NO_x Reduction)	Applicability
Adsorption NO_x/SO_x Removal	Adsorbed NO_x is reduced to N_2 while SO_2 is reduced and condensed to elemental S.	The adsorption process removes NO_x and SO_2 from flue gas by absorbing them onto a special activated char.	40-60% NO_x reduction and 80-95% SO_x reduction.	May be applicable to handle coal.
Electron Beam Radiation NO_x/SO_x Removal	A dry process that utilizes an electron beam to bombard the flue gas, thereby removing NO_x and SO_2.	Flue gas is taken from the boiler air preheater and passed through a cold ESP to remove particulate. NH_3 is added and the gas is then bombarded with an electron beam.	Removal efficiency will decrease as NO_x and SO_2 increase.	By-product (ammonium nitrate and ammonium sulfate powder) treatment technology needs to be more fully developed before commercialization.
Adsorption-Reduction NO_x/SO_x Removal	Simultaneously removes NO_x and SO_2 from flue gas by absorbing them into a scrubbing solution.	Based on the use of Chelating compounds complexed with iron to "catalyze" the absorption of NO_x.	60-70% NO_x reduction and 90% SO_2 reduction.	Applicable only to high sulfur coals.
Oxidation-Absorption-Reduction NO_x/SO_x	Simultaneously removes NO_x and SO_2 from flue gas by oxidizing NO to NO_2 and then absorbing NO_2 and SO_2 into a scrubbing solution.	Based on the use of gas-phase oxidants, either O_3 or ClO_2, to selectively oxidize NO to NO_2.	90% NO_x reduction and 95% SO_2 reduction for oil-fired tests.	Not applicable to low sulfur coals.
Oxidation-Absorption	Excess O_3 is used to selectively oxidize NO_x to N_2O_5.	N_2O_5 formed by oxidation is absorbed into aqueous solution and concentrated to form a 60% HNO_3 by-product.	Not available.	May be applicable to handle high particulate flue gas.

(Continued)

TABLE 4-13. (CONTINUED)

Control Technique	Stage of Development	Secondary Wastes	Costs	Limitations and Comments
Adsorption NO_x/SO_x Removal	Presently in the prototype unit stage of development.	Ash for disposal	20MW estimates: Capital: \$257/kW (coal) Operating: 2.7 mills/kWh (coal)	Very complex process. Numerous process steps involve hot solids handling with numerous mechanical problems possible.
Electron Beam Radiation NO_x/SO_x Removal	No coal-fired tests have been performed at this time.	Ammonium nitrates and sulfates	20MW estimates: Capital: \$241/kW (coal) Operating: N/A (coal)	NO_x/SO_2 removal will drop off drastically at low radiation doses based on oil-fired pilot tests. Sulfate and nitrate salts as well as other ionic species formed as by-products.
Adsorption-Reduction NO_x/SO_x Removal	Preliminary testing stage of development.	Sulfate and nitrate salts and gypsum	20MW estimates: Capital: \$493/kW (coal) \$223/kW (oil) Operating: 8.8 mills/kWh (coal) 6.4 mills/kWh (oil)	Requires large absorbers with high liquid rates. Absorbing solution is highly corrosive; and sulfate and nitrate salts formed as secondary pollutants.
Oxidation-Absorption-Reduction NO_x/SO_x	Prototype stage of development. No coal-fired flue gas tests have been performed at this time.	NO_3^- or N-S salts or NH_3 based compounds in wastewater	20MW estimates: Capital: \$278/kW (oil) Operating: 7.6 mills/kWh	Costly gas-phase oxidants create secondary wastewater pollution problems. The use of ClO_2 introduces a chloride pollutant problem.
Oxidation-Absorption	One coal-fired test has been performed with no published information.	NO_3^- salts in wastewater gypsum	Not available	Production of nitrate salts poses a potential secondary pollution problem. Corrosion problems.

advances have been made; however, some significant technical and economic questions must be answered before widespread application of SCR units can occur.

Particulate Removal

The choice of the particulate collection equipment depends upon a number of factors: the properties of the materials such as particle size and physical and chemical characteristics; the concentration and volume of the particulate to be handled; the temperature and humidity of the gaseous medium; and most importantly the collection efficiency required.

There are four basic types of particulate collection equipment: (1) cyclones, (2) fabric filters/baghouses, (3) venturi scrubbers, and (4) electrostatic precipitators. The key features and unit costs of these collection devices are presented in Table 4-14.

Cyclones are generally employed for the removal of bulk particulates (usually greater than 4 microns in size) and, in many cases, precede other control devices. The unit installed costs of cyclones are relatively low - approximately \$212/m^3 per minute.

Baghouses have very high particulate removal efficiencies and lend themselves to applications involving small or intermittent gas flows. Baghouses, however, have high pressure drops (in comparison with electrostatic precipitators) and cannot ordinarily handle wet gases, gases containing oily materials, or gases having temperatures in excess of 573K. The unit installed cost for a typical baghouse is about \$300/m^3 per minute.

Venturi scrubbers can generally handle gases having temperatures higher than those which can be handled by fabric filters, can operate at high pressure, can tolerate wet and dry gases, and can be very efficient for the removal of submicron particles. In contrast to devices in which the particles are collected in dry form, venturi scrubbers generate a wet slurry which is more voluminous and generally more difficult to dispose of. Unit installed costs for venturi scrubbers are approximately \$250/m^3 per minute.

TABLE 4-14. KEY FEATURES OF PARTICULATE COLLECTION EQUIPMENT

Control Device	Operating Principle	Removal Efficiency Range (weight %)	Inlet Loading Limitation (g/Nm^3)	Normal Pressure Drop Range (cm H_2O)	Reliability or Other Limitations	Secondary Waste	Installed Costs	General Comments
High Efficiency Cyclone	Particulates removed from gas stream by imparting a centrifugal force. The inertia of the particulates carries them to the walls where they fall to the bottom of the cyclone for removal.	50 to 80% for >5 μm. 80 to 95% for 5 to 20 μm.	>2.4	7 to 20	Cannot effectively remove particulates smaller than 5 μm.	Collected particulates	About $212/m^3/min for total installed system.	High reliability due to simple operating principle with no moving parts. Low energy requirements.
Fabric Filter (Baghouse)	Fabric filter material is arranged in a tubular shape with the particulate laden gas stream passing through the filter. Particulate removal primarily results from the buildup of collected material on the dirty-air side of the filter. The filter is periodically cleaned by mechanical shaking or a pressurized reverse air flow.	98.5 to 99.5% for 0.25 to 0.5 μm. 99 to 99.5% for 0.75 to 1 μm. 99.5 to 99.9% for 3 μm. 99.95% for 3 μm.	>0.24	5 to 25	Plugging problems will result if condensation occurs on filter media or if hygroscopic-material is collected. Temperture limit varies with type of filter media used, maximum is 560 K.	Collected particulates	About $282/m^3/min for total system.	High particulate removal efficiency. High installation cost. Large scale required.
Venturi Scrubber	Removal of particulates from a gas stream by intimate contact with multiple jet streams of scrubbing water and droplets. Agglomerated particulates are subsequently removed in a centrifugal and/or mist eliminator.	50 to 92.5% for 0.25 μm. 60 to 98% for 0.5 μm. 70 to 99% for 0.75 μm. 90 to 99.6% for 3 μm.	>0.5	13 to 250	Reliability may be limited by scaling, fouling, or corrosion. Scrubbing liquor blowdown may require treatment or contain potentially valuable material not directly recoverable.	Scrubbing liquor blowdown and wet slurry	About $250/m^3/min (increasing cost with increasing removal efficiency).	High particulate removal efficiency. Capable of treating streams with wide ranges in temperature (no limitation for high temperatures), pressure, and gas composition. High efficiencies require high energy consumption.
Electrostatic Precipitator	A negative electrical charge is imparted to the particulates and they are collected on positively charged plates. Collected material is removed by periodically rapping or vibrating the collection plates.	95 to 99% for 0.1 μm. 90 to 96% for 0.5 μm. 95 to 99% for 1 μm. 99 to 99.9% for 5 μm.	0.24	0.5 to 2.5	Not applicable to combustible or potentially explosive mixtures. Particulates to be collected must have suitable electrical resistivity to facilitate efficient removal. Used in low pressure applications. Limited to gas streams with temperatures below 700K.	Collected particulates	About $250 to $530/m^3/min (increasing cost with increasing removal efficiency).	High particulate removal efficiency, especially the sub-micron range. High capital and installation cost. Very low pressure drop. Suitable for high temperature or large volume applications. High electrical consumption. Sensitive to particulate resistivity.

Electrostatic precipitators are high efficiency particulate removal devices, have low pressure drops, are capable of handling large volumes of gases, and can tolerate high feed gas temperatures. Electrostatic precipitators, however, are not generally suitable for applications to gases above atmospheric pressure and are not economical for treating small or intermittent gas flows (such as those resulting from material handling dust collection systems). Unit installed costs range from \$250 to \$530/m^3 per minute.

SO_2 Removal

Several flue gas desulfurization (FGD) processes are commercially available. They are basically of two types: (1) throwaway systems which produce a waste sludge, and (2) regenerable systems which produce a usable sulfur by-product and regenerate the sorbent. Common examples of throwaway systems are the lime/limestone system, dry scrubbing, double alkali scrubbing, fly ash alkalinity scrubbing, and Chiyoda Thoroughbred 121. Typical examples of regenerable systems are the Wellman-Lord and magnesium oxide processes. Key features of some of these scrubbing systems are presented in Table 4-15.

The lime/limestone scrubbers are the most commonly employed throwaway systems for electric utility applications. In the lime/limestone process, solid lime or limestone is pulverized and mixed with water to form a scrubber liquor which contacts the flue gas in an absorption tower where calcium sulfate and calcium sulfite are formed. The resulting slurry is removed from the system and treated, and the sludge resulting from slurry treatment is disposed of. Scrubbing solution is recovered and recycled to the absorption tower. SO_2 removal efficiencies can approach 90% by carefully balancing the many chemical reaction parameters involved in the lime/limestone FGD process. Of the throwaway FGD systems available, lime/limestone offers the least complex system and equipment, the easiest pH control, and the cheapest raw materials. Operating experience has indicated that careful attention to system control is important for successful operation of lime/limestone FGD systems.

Of all the commercially available regenerable FGD systems, Wellman-Lord is the most extensively used. A venturi prescrubber often precedes the Wellman-Lord absorber to remove residual particulates from the flue gas and avoid ash accumulation in the absorber. Sulfur dioxide is absorbed by an alkaline sodium sulfite solution to produce primarily sodium bisulfite. This bisulfite-rich solution is then pumped to a forced-circulation vacuum

TABLE 4-15. KEY FEATURES OF SO_2 REMOVAL PROCESSES

Process Feature	Lime/Limestone Scrubbing	Double Alkali Scrubbing	Chiyoda Thoroughbred 121	Wellman-Lord	Dry Scrubbing	Fly Ash Alkalinity Scrubbing
Principle	Liquid phase absorption of SO_2 in lime or limestone slurry.	Liquid phase absorption of SO_2 in a sodium hydroxide, sodium sulfite, sodium bisulfite, sodium sulfate, and sodium carbonate solution. Regeneration of the sodium sulfite/bisulfite with lime in a reactor. A dilute mode can be used for concentrations of 200-1500 ppm SO_2 and where less than 25% oxidation of sulfite to sulfate occurs. Concentrated mode can be used for concentrations of 1000-8000 ppm SO_2.	Liquid absorption of SO_2 in a single vessel, where limestone addition and dissolution, air oxidation, and gypsum precipitation occur.	Liquid phase absorption of SO_2 in a sodium bisulfite, sodium sulfite, and sodium carbonate solution. A rich SO_2 is produced by evaporation, which is then processed in a Claus unit to produce elemental sulfur or in a sulfuric acid plant.	Process involves the use of a spray dryer which contacts the flue gas with an aqueous alkaline material and produces a dry product. System involves two stages: 1st stage-spray dryer; 2nd stage-dry particulate collector which removes flue ash and reaction product fron flue gas.	Process involves a two stage venturi-spray tower absorber utilizing the fly ash alkalinity for SO_2 removal. Hydrated dolomitic lime, ($Mg(OH)_2$ and $Ca(OH)_2$) is also used to achieve an outlet SO_2 of 43 ng/J.
Feed Stream Requirements	Particulates can be removed in an ESP or fabric filter to achieve 99⁺% at lowest energy consumption. Fly ash may be removed in a venturi where the fly ash contains significant alkalinity. A scrubber can be used for both high particulate and SO_2 removal.	Excessive particulates should be removed in an ESP, fabric filter or venturi. O_2 should be less than 7% for concentrated mode.	Particulates and chlorides should be removed from inlet flue gas if byproduct gypsum is to be sold.	Particulates and chlorides must be removed from flue gas.	Inlet SO_2 concentration should not exceed 1000 ppmv.	Venturi is used to remove particulates and a portion of SO_2.
Absorbent	Slaked lime or 200-300 mesh limestone 6-12% slurry circulated.	Sodium hydroxide, sodium sulfite/bisulfite, and a small amount of sodium sulfate.	Limestone slurry.	Concentrated sodium sulfite/bisulfite.	Lime slurry or sodium carbonate solution.	Fly ash alkalinity and hydrated lime (calcium and magnesium hydroxide).
Product/ Waste	Gypsum can be produced with forced oxidation. Calcium sulfate/sulfite can be produced with 50-70% solids.	Filter cake with 60-70% solids, primarily calcium sulfite and calcium sulfate.	Gypsum ($CaSO_4 \cdot 2H_2O$) with less than 20% moisture content.	Concentrated SO_2 purge stream (90% SO_2).	Sodium sulfite-sodium sulfate; calcium sulfite/ sulfate.	Sludge consists of fly ash, gypsum ($CaSO_4 \cdot 2H_2O$), $Mg(OH)_2$, small amount of calcium sulfite.
Efficiency	90% removal can be obtained generally for low and high sulfur coals. Higher removals can be obtained with higher L/G and pressure drop, and to some extent scrubber type. 90% and greater can be obtained for low sulfur coals. 95% removal for high sulfur coals when adipic acid is used. Commercially demonstrated in over 30 FGD units.	90-99% removal can be obtained for low and high sulfur coals. Concentrated mode has been demonstrated at Louisville Gas & Electric's 200 MW coal fired boiler. Smaller industrial units (General Motors) have been operated in the dilute mode.	90% SO_2 removal or outlet SO_2 equal to 300 ppmv. Process has been demonstrated at Gulf Power's Scholz station - 20MW prototype.	Process has been demonstrated in a NIPSCO 115MW coal fired boiler. Can remove up to 95% SO_2.	70% SO_2 removal using lime as absorbent. 80% SO_2 removal using sodium absorbent.	85-90% removal of SO_2 commercially demonstrated in Montana Power's Colstrip 1 & 2. 96⁺% expected in Colstrip units 3 & 4.

(Continued)

TABLE 4-15. (CONTINUED)

Process Feature	Lime/Limestone Scrubbing	Double Alkali Scrubbing	Chiyoda Thoroughbred 121	Wellman-Lord	Dry Scrubbing	Fly Ash Alkalinity Scrubbing
Cost*	Capital - $90/kW to $185/kW.	Capital - $101/kW to $163/kW.	Capital - $160/kW.	Capital - $138/kW to $265/kW.	Capital - $23/kW to $47/kW.	Not available.
Advantages	Lower capital cost and O&M costs. SO_2 and particulates can be removed simultaneously. Relatively simple process. Reliability is 90-95 .	Lower capital and O&M costs. SO_2 can be removed to very high efficiencies (99). Reliability is 90-95 . Conventional process equipment.	Capital and O&M costs appear to be competitive but data limited to prototype experience. Potential saleable gypsum by-product.	Commercially demonstrated. Process produces saleable product sulfur with a Claus unit or sulfuric acid. Lower potential for scaling than calcium system.	Lower projected operating and capital costs. Dry product.	Commercially demonstrated in 300MW units. Sludge contains little calcium sulfite which improves dewatering and therefore reduces settled water content. Less potential for scaling.
Disadvantages	Process produces approximately 2 times (by wt) sludge as ash collected. Sludge can be thixotropic. Sludge quantities can be reduced by forced oxidation.	Process produces 1.5 times (by wt) filter cake as collected ash. 316SS material of construction may be required to prevent corrosion and pitting.	Process has not been demonstrated commercially in a 100MW or larger unit.	High utility costs (steam) compared to other systems. Special metallurgy may be required. System required to process SO_2 to sulfur or sulfuric acid.	Process will not be commercially demonstrated until late 1982. Product disposal could be a problem when sodium salts are used as absorbent.	Process is generally applied to coal fired boilers which burn high alkalinity coal.

evaporator where it is indirectly heated by steam to convert the bisulfite to sulfite and gaseous SO_2. A portion of the sodium sulfite is also converted irreversibly to sodium sulfate and thiosulfate which must be purged from the system, requiring a makeup of NaOH or $NaCO_3$. The Wellman-Lord process can achieve over 90% SO_2 removal.

Dry scrubbing experience to date has been limited, although systems that have been operated show much promise, especially for low- and medium-sulfur coals (79). The Spray Drying process is the only dry scrubbing process currently being offered commercially. In this process the absorbent solution, usually either lime or soda ash, is atomized and sprayed into the incoming flue-gas stream to increase the liquid/gas interface and promote mass transfer between the SO_2 and the slurry droplets. Simultaneously, the thermal energy of the gas stream evaporates the water in the atomized droplets to produce a dry, powdered mixture of sulfite/sulfate and unreacted reagent. When used in combination with fabric filters these systems have performed extremely well. The fabric filter collects the particulates and also recovers some of the expensive reagent which is reused. In addition, unused reagent that cakes on the fabric is available to react with more SO_2 as flue gas passes through it.

FGD costs for boilers in synfuel plants depend upon the amount of sulfur emissions control required. This may vary depending upon the amount of sulfur in the fuel. FGD cost data have been developed by the EPA for electric utility steam generating units ranging in size from 25 MW_e to 1000 MW_e. The cost variations are principally governed by (1) size of the boiler, (2) coal used, (3) averaging time over which the plant must meet SO_2 limitations, and (4) the level of control maintained. Capital investment and annual operating costs for lime/limestone and Wellman-Lord FGD systems are listed in Table 4-15. These costs are for a 500 MW_e unit boiler burning 3.5% sulfur bituminous coal capable of achieving 90% removal.

4.1.2.1 Boiler Flue Gases (Stream 302) - Individual Stream Control

Steam requirements for process and electric power generation purposes for the K-T based methanol plant are assumed to be met by the boiler coal feed rate of 25,230 kg/hr (as received basis). A material balance for the Illinois No. 6 coal fired boiler was previously presented in Table 3-26. The offgases from the boiler were estimated to have a flow rate of 10,385 kmol/hr and contain 0.21 and 0.036% by volume of SO_2 and NO_2, respectively. The uncontrolled particulate emissions were estimated to be 2421 kg/hr. These emission rates were estimated to increase by 215% for the Fischer-Tropsch synthesis case and decrease by 48% for the Mobil-M synthesis case.

In this section, details of pollution control alternatives applicable to the 25,230 kg/hr Illinois No. 6 coal fired boiler are examined. However, it is possible that some of the steam requirements of the pulverized coal fired boiler may be offset by the combustion of dewatered dust from gasification. If dewatered dust is burned to generate steam, coal requirements of the pulverized coal fired boiler for the K-T based methanol plant will decrease by approximately 8900 kg/hr. Details regarding combustion of dewatered dust are provided in Section 4.3. For the purposes of discussion in this section, the offset in steam production from dewatered dust combustion will be ignored.

The control of NO_x, SO_2, and particulate emissions from the Illinois No. 6 coal fired boiler is expected to present no unique problems over those encountered in the electric utility and other industries which use coal fired units. The applicability, performance, and costs of these controls for the pulverized coal fired boiler are discussed below.

NO_x Control

As discussed earlier, NO_x control in boilers is achieved through both the design and operation of the combustion units to minimize its formation. For new pulverized coal fired boilers this is achieved primarily by the use of either low NO_x burners (LNB) or overfire air (OFA). Boiler manufacturers have used LNB or OFA as standard equipment on new boilers since the early 1970's (85). Therefore, there are no incremental costs for NO_x control equipment since no new boilers can be purchased from U.S. manufacturers without these controls, regardless of whether the boiler is being built in the U.S. or abroad. However, retrofitting NO_x control equipment on older boilers does have cost implications. These costs would be site specific and will also depend upon the type of NO_x control technique utilized. Since new K-T gasification facilities will employ new boiler units, retrofit costs for NO_x controls are not discussed in this manual. However, these costs can be obtained from several EPA documents (83,84).

Particulate Removal

Particulate loading in boiler flue gases is a function of many variables such as the type of coal being fired, the amount of ash in the coal, and the boiler design. Typically, 60 to 80% of the feed coal ash is emitted as fly ash. For the Illinois No. 6 coal under consideration in this document, the uncontrolled particulate emission rate for the methanol synthesis case was estimated to be 2421 kg/hr.

Usually electrostatic precipitators or baghouses are used for particulate emission control from coal fired boilers. In utility applications electrostatic precipitators are more widely used than baghouses at the present time.

The only secondary waste streams from particulate control devices are the collected particulate from the boiler flue gas (Stream 423). Typically 99% of the uncontrolled particulates in the flue gas stream are collected. Varying degrees of control for trace elements are also achieved with particulate control, depending primarily on the volatility of the individual elements and on the efficiency of particulate control. For the size K-T based methanol plant under consideration, this waste dust will be generated at a rate of approximately 2400 kg/hr. In the case of both the ESP and baghouse the collected particulates are dry. Therefore, it is possible that fugitive particulate emissions may be generated during transfer and conveying from control device to solid waste storage. The control of fugitive particulate emissions during conveying and transfer is discussed in Section 4.1.6.

Costs for ESPs depend primarily upon the flue gas particulate loading and the flue gas flow rate. To achieve outlet loadings of less than 45 ng/J for the base plant boiler, over 99% particulate removal is desired. For a combustion flue gas flow rate of 10,385 kmol/hr, the capital investment to achieve outlet particulate loadings of 14 ng/J and 43 ng/J are estimated to be $6.1 million and 4.8 million, respectively. The annualized costs for the same particulate loadings are estimated to be $1.2 million and $0.9 million, respectively. These costs correspond to 0.55 and 0.43% of the base plant capital investment and 0.35 and 0.27% of the base plant annualized costs. The limited cost data on ESPs indicate that ESP capital investment costs vary proportionally with flue gas flow rate provided all other variables remain the same.

SO_2 Removal

As discussed previously, a number of competitive FGD processes are capable of achieving similar SO_2 reductions. However, lime/limestone and Wellman-Lord FGD processes are the most widely used SO_2 control processes in the industry today. The costs for these systems vary greatly depending upon the boiler size, coal sulfur content, and the degree of SO_2 removal desired.

The pulverized coal-fired boiler associated with a K-T based methanol plant utilizing Illinois No. 6 coal has approximately 21.95 kmol/hr (0.21%) of SO_2 in the flue gas. Assuming that 83% SO_2 removal is desired (outlet concentration of 370 ppmv), a lime-limestone FGD system will require a capital investment of approximately \$23.3 million with annual operating costs of about \$5.32 million. Alternatively, it is estimated that a Wellman-Lord system will require a capital investment of \$22.5 million with annual operating costs of \$4.9 million. These costs correspond to 2.1% of the base plant capital investment and 2.7% of the base plant annualized cost for the lime/limestone FGD. In the case of the Wellman-Lord, the costs are 2% of the base plant capital investment and 2.5% of the base plant annualized cost. Capital investment and annual operating costs would increase by approximately 5% had 90% SO_2 removal been the design target.

Sludges and brines are generated by the lime/limestone and Wellman-Lord FGD systems. For the specific size K-T based methanol plant under consideration, the lime/limestone FGD system is estimated to produce 10,722 kg/hr of moist waste sludge (Stream 424). Alternatively, a Wellman-Lord FGD system is estimated to produce 550 kg/hr of sulfur product (Stream 426) and a thiosulfate/sulfate by-product purge stream (Stream 425) of 150 kg/hr.

4.1.2.2 Process Heater Flue Gases - Individual Stream Control

Process heaters in a K-T gasification facility are expected to utilize either offgases or liquid products from synthesis/fractionation operations. The offgases and liquid fuels are essentially free of sulfur, particulate, and fuel bound nitrogen. Therefore, the contribution of process heaters to sulfur and particulate emissions is minimal. Any NO_x emissions generated are a function of combustion design, and combustion modification techniques discussed previusly are applicable.

Control of NO_x emissions from process heaters has been investigated in recent years. Initial data indicate that load variation, staged combustion, and low NO_x burners can be used to control NO_x emissions. Cost information on these techniques is very site-, size-, and fuel-specific. The number and size of process heaters for a K-T gasification facility depend upon the details of process heat requirements. Since it is beyond the scope of this document to perform the detailed engineering required to assess these requirements, no detailed cost estimation for the control of NO_x emissions from specific process heaters was performed. However, cost information from vendors indicates that low NO_x burners may cost approximately $0.95/MJ when applied to process heaters (86).

4.1.2.3 Secondary Streams from Other Media - Fluidized-Bed Boiler Flue Gases (Stream 413) - Individual Stream Control

As discussed in Section 3.3.1, a filtration step has been included in the design for the gas cooling and dust removal process. In the case of bituminous coal gasification, this filtration step may be desirable to reduce pond area and/or improve the feasibility of dust combustion prior to disposal. In this section details of pollution control alternatives applicable to the combustion flue gases from the fluidized bed combustion of dewatered dust (see Section 4.3) are discussed. The flow rate of the flue gas from the fluidized-bed boiler is estimated to be 7419 kmol/hr. It is estimated to contain 0.18% SO_2 by volume and 1846 kg/hr of particulates. NO_x emissions are estimated to be about 150 ng/J. The composition of the flue gas is presented in Table 4-16.

TABLE 4-16. COMPOSITION OF FLUE GAS FROM THE DEWATERED DUST-FIRED FLUIDIZED-BED BOILER (STREAM 413)*

Components	Flue Gas Composition (Dry Basis) mole %	kg/hr	kmol/hr
N_2[†]	59.5	123,664	4415
H_2O	23.9	31,916	1773
CO_2	12.0	39,278	892
O_2	3.7	8,746	273
SO_2	0.18	838	13
Ar	0.71	2,109	53
	100.0	206,551	7419
Solids[‡]		1846	

*Flue gas flow rates are based upon engineering estimates.

[†] NO_x is approximately 150 ng/J which is equivalent to 56 kg/hr (as NO_2).

[‡] Before final particulate control.

NO_x Control

Almost all the data from fluidized-bed boilers indicates NO_x emission levels of less than 301 ng/J (87). For a fuel containing only 36% carbon by weight (dry), these emissions will be even lower, around 150 ng/J. Since these emission levels are relatively low for coal fired boilers, no NO_x controls for the fluidized bed boiler are likely to be used.

Particulate Control

Particulate matter emitted from the combustion section of a fluidized-bed boiler consists of fly ash from the coal, unburned carbon, and elutriated bed material. A primary cyclone is used to collect larger particles containing the most significant carbon concentration for circulation back to the fluidized-bed combustor or to a separate carbon burnup cell. A secondary cyclone of higher efficiency can also be used to collect smaller particles for disposal as ash. Approximately 90% of the particulate matter is captured prior to final particulate control.

Final particulate control after primary and/or secondary cyclones is performed by use of conventional systems previously discussed in Section 4.1.2. The systems can consist of electrostatic precipitators, fabric filters, scrubbers, or cyclones. They can be operated as hot-side or cold-side units (upstream or downstream of final heat recovery), except for fabric filters which must be installed cold-side to prevent excessive fabric deterioration. Existing fluidized bed units typically use either fabric filters or electrostatic precipitators (87).

Costs for particulate control were estimated assuming the particulate control device used is an electrostatic precipitator. For 99.7% particulate removal, the capital investment for the ESP unit was estimated to be $4.4 million for a flow rate of 7419 kmol/hr (refer to Table 4-16). Annualized costs were estimated to be $0.9 million. These costs correspond to 0.4% of the base plant capital investment and 0.26% of the base plant annualized cost.

SO_2 Removal

Sulfur dioxide emissions are a major concern in conventional coal-fired boilers. However, by using fluidized-bed technology, SO_2 emissions can be reduced by up to 90% or more by direct addition of sorbent into the bed. The coal is burned in the presence of lime sorbent. The SO_2 reacts with the calcium oxide and excess oxygen forming calcium sulfate. The degree of SO_2 capture is strongly dependent on the calcium to sulfur molar feed ratio. Other factors which affect the sulfur capture efficiency of the system are the reactivity of the sorbent, the particle size of both sorbent and coal, gas residence time in the bed, the feed mechanism and material distribution in the bed, and temperature. These parameters can be adjusted to obtain the maximum SO_2 removal for the system at a particular Ca/S molar feed ratio. Past data indicate that an average Ca/S molar feed ratio of between about 2.5 and 4 will achieve a reduction of 90% in SO_2 emissions, depending upon the sorbent reactivity; however, higher ratios may be needed if sorbents of low reactivity are used (87).

Capital investment and annualized costs for controlling SO_2 emissions are included in the costs of the fluidized-bed boiler. Capital investment and annualized costs for the fluidized boilers are discussed in Section 4.3 Past data indicate that the percent increase in costs for fluidized boilers capable of achieving 85% SO_2 removal over uncontrolled conventional boilers (49 MW_t capacity) burning 0.9% sulfur coal is approximately 5 to 7% (87).

4.1.3 Organic and CO Containing Waste Gases

There are two major waste streams which are free of sulfur compounds but contain appreciable levels of organics and/or CO: (1) CO_2 offgas from SNG purification (Stream 239) in F-T synthesis; and (2) Mobil M-gasoline synthesis catalyst regeneration/decommissioning offgases (Stream 231). In addition, an offgas containing CO may be generated as a result of decommissioning methanation catalyst (Stream 237) in facilities employing F-T synthesis. In the event that these waste gases warrant control of organic and/or CO emissions, controls such as thermal or catalytic incineration may be applicable. Flaring is typically employed for small volume, intermittent gases or gases resulting from upset conditions and would not be appropriate for treatment of SNG purification offgas or the Mobil catalyst regeneration/decommissioning offgases. Key features of these incineration processes are discussed in Section 4.1.1.

In an integrated facility, waste gases discussed in this section might be combined with other waste gases for incineration in a common incinerator. However, because of the limited characterization and generation rate data for waste gases, cost estimates in this section are presented in terms of dedicated incineration units. Therefore, these control costs represent upper limit costs for control of these streams due to the economy of scale which might result if waste gases can be combined for incineration.

4.1.3.1 CO_2 Offgas from SNG Purification (Stream 239) - Individual Stream Control

Facilities employing F-T synthesis with SNG co-production will generate a CO_2-rich offgas (Stream 239) on a continuous basis as a result of SNG purification. This offgas will consist primarily of CO_2 and would be free of sulfur compounds although it may contain appreciable concentrations of organics and CO. For purposes of evaluation, the offgas has been estimated to contain 1% CH_4, 0.2% non-methane hydrocarbons, and traces of CO (see Section 3.4.6). The total flow rate of this stream was estimated to be approximately 273 kmol/hr. Control of potential CO_2 offgas emissions by incineration is discussed in this section.

Incineration

The CO_2 offgas from SNG purification is estimated to contain approximately 4.3 kmol/hr total hydrocarbons (expressed as CH_4). Thermal incineration of organic-containing waste gases and liquids is reported to result in flue gas concentrations ranging from <5 to 70 ppmv total hydrocarbons (expressed as CH_4), and 7 to 89 ppmv CO. Assuming flue gas concentrations of 30 ppmv total hydrocarbons and 50 ppmv CO, thermal incineration of the CO_2 offgas using a low Btu supplemental fuel gas would result in emissions of approximately 0.01 kmol/hr total hydrocarbons (expressed as CH_4) and 0.02 kmol/hr CO. The total capital investment for this thermal incinerator would be approximately $296,000. Annualized costs would be $100,000. These costs correspond to 0.02 to 0.03% of the base plant capital investment and the annualized base plant costs. Similar performance and costs would be associated with the catalytic incineration alternative.

4.1.3.2 Regeneration/Decommissioning Offgases (Streams 231 and 237) - Individual Stream Control

There are two sources of offgases resulting from catalyst regeneration and/or decommissioning. Facilities employing Mobil M-gasoline synthesis will generate an offgas from regeneration/decommissioning of the synthesis catalyst (Stream 231), while facilities employing F-T synthesis with SNG co-production may generate an offgas when decommissioning the methanation catalyst (Stream 237). The Mobil M-gasoline synthesis catalyst requires periodic regeneration for coke removal. For the subject facility, it has been estimated that regeneration will occur over a period of 3800 hours per year, and offgases will be generated at an average rate of 200 kmol/hr. This offgas is likely to contain hydrocarbons and/or CO. Methanation catalysts are not typically regenerated but, because they tend to be pyrophoric in the active state, they are oxidized during decommissioning. No data which enable the estimation of methanation catalyst decommissioning offgas flow rates or characteristics are available.

Control of potential Mobil M-gasoline catalyst regeneration/decommissioning offgas emissions by incineration is discussed in this section. Control of offgases from methanation catalyst decommissioning will not be addressed due to data limitations. However, in principle, control of organic/CO emissions associated with methanation catalyst decommissioning could be achieved by thermal or catalytic incineration or by flaring.

Incineration

Thermal incineration of organic-containing waste gases and liquids is reported to result in flue gas concentrations ranging from <5 to 70 ppmv total hydrocarbons (expressed as CH_4) and 7 to 89 ppmv CO. Although characterization data are not available for offgas from Mobil M-gasoline synthesis catalyst regeneration, hydrocarbons and/or CO may be present in the incinerator feed gas due to the offgas composition or the fuel gas composition. Assuming fuel gas concentrations of 30 ppmv total hydrocarbons and 50 ppmv CO, thermal incineration of the Mobil M-gasoline synthesis catalyst regeneration/decommissioning offgas would result in emissions of approximately 0.01 kmol/hr total hydrocarbons and 0.02 kmol/hr CO. These estimates are based upon the assumptions that the offgas would not have significant heating value and that a low Btu fuel gas would be employed as supplemental fuel. The capital investment for this thermal incinerator would be approximately $289,000. The annualized costs would be $90,000. These costs correspond to 0.02% to 0.03% of the base plant capital investment and the annualized base plant costs, respectively. Similar performance and costs would be associated with the catalytic incineration alternative.

4.1.4 Fugitive Dust from Material Storage (Stream 200)

Open or partially enclosed storage piles are often used for storage of bulk materials not affected by precipitation or slight contamination such as coal, sand, gravel, clay, and gypsum. The material may be stored for a short time with a high turnover rate to accommodate surges in daily or weekly rates of sequential processes or may provide a long-term reserve for emergency supply or to meet cyclical seasonal demands.

Most dust arises from stockpile areas as the material is dumped from the conveyor or chute onto the pile and as material is reclaimed from the pile. During periods of high wind speeds or low moisture, wind erosion of the surface may also cause emissions.

In coal gasification/liquefaction plants fugitive dust is emitted by coal and solid waste storage piles. The techniques used to control these emissions are not unique to liquefaction plants and are widely used in industries that require large scale material storage. The most commonly used techniques are vegetative stabilization, chemical stabilization, capping, stacked segregation, water spraying, and confinement. Surface protection methods such as vegetative stabilization, chemical stabilization, capping, and stacked segreation are primarily used on reserve storage piles since these piles are subject to minimal disturbances. Active storage piles generally require either water spraying or confinement to control dust emissions. The key features and unit costs for these techniques are listed in Table 4-17.

Vegetative stabilization involves planting an appropriate ground cover or shrub over the pile to be stabilized. A soil cap may be required to support vegetation. The efficiency of vegetative cover in reducing wind erosion is dependent on the density and type of vegetation that can be grown. For applications such as stabilizing tailing piles, the use of vegetative stabilization decreases emissions approximately 65%. When vegetative stabilization

TABLE 4-17. KEY FEATURES OF STORAGE PILE DUST CONTROL TECHNOLOGIES

Method	Control Principle	Control Effectiveness*	Reliability/ Special Problems	Unit Costs*	Other Pollutants Generated
Vegetative Stabilization	Covering pile with sod.	Approximately 65% reduction over unstabilized pile; and 90% if chemical stabilizer is also used.	1. Requires frequent watering. 2. Handling of sod during reclamation operations is cumbersome and expensive. 3. Upper layer of stored material is contaminated with soil.	\$2.70/m^2	Soil dust from earth covering.
Chemical	Wetting Agents Modify surface tension properties to improve effectiveness of water sprays.	Up to 90% reduction in dust losses.‡	1. Piping may require heat tracing when freezing is a concern. 2. Can cause corrosion problems in equipment exposed to sprays. 3. May increase material degradation. 4. Effects are short-term.	\$.33-.77/Mg†	Volatiles which depend on wetting agent utilized.
	Crusting Agents Organic binders combine with particles to form tough crust on surface.	Up to 90% reduction in dust losses.	1. May increase chances of spontaneous combustion, especially in piles subject to stockpile and reclaim operations. 2. Crust tends to break up during heavy rains.	\$.55- .72/m^2	Volatiles which depend on crusting agent utilized.

(Continued)

TABLE 4-17. (Continued)

Method	Control Principle	Control Effectiveness*	Reliability/ Special Problems	Unit Costs*	Other Pollutants Generated
Capping	Paving with earth or asphalt or cover with polyethylene.	Up to 100%.[†]	1. Both coverings may increase chances of spontaneous combustion. 2. Polyethylene presents severe handling problems and is also not practical in high wind climates.	$.49/m^2 for asphalt. $1.96/m^2 for polyethylene.	Soil dust from earth covering.
Stacked Segregation	Coating surface of compacted storage pile with layer of select, medium sized material.	No data available.	Either deliveries of different sized material must be coordinated or both sizes must be readily available from storage.	Not available	none
Water Spray	Spray application of 210-250 L/Mg to reduce dusting.	Approximately 50% reduction in losses.	1. Piping may require heat tracing when freezing is a concern. 2. May increase degradation. 3. Frequent re-treatment necessary.	Not available	none
Confinement	Enclosure of active storage pile in a totally enclosed barn or silo with point source dust control equipment on building vents.	Up to 99% reduction in losses.	Requires extreme care when storing potentially explosive materials.	$110/Mg of stored material $1 million to $3 million per silo depending on size.	none

*Cost and control efficiency data obtained from Reference 88

[†] Data obtained from Reference 89

[‡] Data obtained from Reference 90

is used in conjunction with a chemical stabilizer, this efficiency increases to approximately 90%.

Chemical stabilization to decrease fugitive dust emissions involves the application of wetting or crusting agents. Wetting agents are used to provide better wetting of fines and longer retention of moisture. They also reduce the water surface tension allowing the fines to be wetted with a minimum amount of water. This treatment protects stockpiled material until the added moisture is removed by heat and wind. Some of these agents remain effective for weeks or months without additional rewatering depending on local conditions. Crusting procedures involve the use of bunker C crude oil, water soluble acrylic polymers, or organic binders. These materials are sprayed on the surface of the storage pile, coating the top layer of particles with a thin film. This film causes the particles to adhere to one another, forming a tough durable crust which is resistant to wind and rain. As long as the crust remains intact, the storage pile is protected from wind losses.

Capping involves the paving of the surface area of the storage pile with asphaltic compounds or earth or covering the pile with polyethylene tarpaulins. Usually a slurry of wood pulp and asphalt or road tar is sprayed over the surface of the pile. The covering is usually about 3 mm thick. Polyethylene tarpaulins are also used, however, they are cumbersome to handle when there are high wind speeds or when a large size storage pile is to be capped.

Another effective means of controlling dust emissions from coal storage piles is the stacking of coarse material on the surface of a properly compacted pile. For instance, a 0.152 m layer of fine coal (6.4mm x 0 mm) on the top and sides of the coal storage pile can be anchored in place by a 0.102 m layer of larger size coal (24 mm x 0 mm) placed on top of the fine coal. The larger size coal has better weathering characteristics compared to the smaller sized coal.

Water spraying is another common method of dust suppression. Dust control by water spraying is usually obtained by placing spray nozzles at strategic locations over the stockpile area. The spraying operation is simple in that it only involves the operation of a pump. Water requirements for large volume operations vary from 210 to 250 liters/Mg of material. Such systems are, however, prone to freezeups during winter months. Also, the added moisture can create handling problems during reclamation and subsequent processing.

Enclosure of the coal storage pile is generally the most effective means of reducing fugitive dust emissions, because it allows the emissions to be captured. However, enclosures can be very expensive, since they have to be designed to withstand wind and snow loads and meet requirements for interior working conditions. An alternative to enclosure of all material is to screen the material prior to storage, sending the oversize material to open storage and the fines to enclosures.

4.1.5 Fugitive VOC Emissions

There are many sources of fugitive VOC emissions in a synthetic fuel plant. These emissions can be categorized as (1) evaporative emissions that result from the storage of liquid products and by-products and (2) VOC emissions that result from fluid leaks from plant equipment.

Evaporative Emissions

Evaporative emissions from storage tanks storing volatile liquids result from temperature changes which cause the vapor pressure of the stored liquid to vary, causing vapor emissions. The minimum accepted standard for storage of VOC is the fixed roof tank. It is designed to operate at only slight internal pressure or vacuum and is susceptible to emissions from thermal expansion and other mechanisms by which vapors are produced.

Emissions from fixed roof tanks can be reduced by minimizing diurnal temperature variations (e.g., placing tanks underground), proper setting and maintenance of pressure vacuum vents, and leak prevention efforts. Significant controls can be effected by either floating a cover on the surface of the stored liquid or by replacing the fixed roof storage tank by a floating roof storage tank.

Floating roof tanks successfully limit hydrocarbon losses by eliminating the ullage into which stored material vaporizes. This is accomplished by floating a rigid deck or roof on the surface of the stored liquid thus eliminating air space and preventing the formation of organic vapor above the liquid surface. To effectively control emissions, the floating roof employs primary and secondary seals to shelter the liquid surface from the atmosphere. Control efficiencies of greater than 90% are achievable by floating roof tanks.

Vapor processing units can also be used to control VOC emissions from fixed roof storage tanks. Some of the vapor processing techniques available are carbon adsorption, thermal oxidation, refrigeration, compression-refrigeration-absorption, and compression-refrigeration-condensation. Catalytic oxidation is not typically employed in this application.

The carbon adsorption vapor recovery unit uses beds of activated carbon to remove VOCs from the air-vapor mixture. These units generally consist of two vertically positioned carbon beds and a carbon regeneration system. The air-vapor mixture enters the base of one of the adsorption columns, and the VOC components are adsorbed onto the activated carbon as the gases ascend. Adsorption in one carbon bed occurs for a specific timed cycle before switch-over to desorption. The nearly saturated carbon bed is then subjected to vacuum, steam, or thermal regeneration, or a combination of these methods, and the VOCs are stripped from the bed. Vacuum regenerated units recover VOCs by absorption in a product stream which circulates between the control unit and product storage. The air and any remaining VOCs exiting from the absorber are passed again through the absorbing bed and exhausted to the atmosphere. Steam regenerated units condense the VOC-water mixture and return the separated product to storage.. Some vacuum regenerated systems remain in operation for up to two hours after loading activity ceases, in order to collect any residual vapors in the system and to assure complete regeneration of the carbon beds.

Thermal oxidation units rely upon burning VOC vapors to produce nonpolluting combustion products. Vapors are piped either to a vapor holder or directly to the oxidizer unit. When a vapor holder is used, operation of the oxidizer begins when the holder reaches a preset level and ends when the holder is empty or at the lower preset level. With no vapor holder in the system, the oxidizer is energized by means of pressure in the vapor line, or by an electrical signal produced by manual activation. In some cases propane is injected into the vapor stream to keep the VOC level above the explosive level.

Refrigeration type recovery units remove VOCs from an air-vapor mixture by straight refrigeration at atmospheric pressure. Vapors displaced from storage tanks enter a condenser section where methylene chloride "brine" is pumped through the finned tube sections of a heat exchanger. Brine temperature in this section ranges from 190K to 210K. Some units contain a precooler section (glycol and water solution circulating at 274K) to remove most of the water from the gases prior to the main condenser. There are no compression stages in this type of unit. The condensed product is collected and pumped to one of the product storage tanks. The cold collection surfaces are periodically defrosted by pumping warm (305K) trichlorethylene through the condenser. This defrost fluid is kept warm by heat salvaged from the refrigeration equipment. Recovered water passes to a waste storage tank or gasoline-water separator. The defrost cycle takes from 15 to 60 minutes, depending on the amount of ice accumulated on the finned-tubes.

In a compression-refrigeration-absorption (CRA) vapor recovery system, the vapors from the product storage tanks are first passed through a saturator which sprays liquid product into the air-vapor gas stream. This ensures that the VOC concentration is above the explosive range. The saturated gas mixture is stored in a vapor holder until, at a preset level, it is released to the control unit. The vapor holder is usually a special tank containing a bladder with variable volume and constant pressure. A product storage tank with a lifter roof can also function in this capacity.

The first stage of CRA processing is a compression-refrigeration cycle in which water and heavy VOCs are compressed, cooled, and condensed. The uncondensed vapors move into a packed absorber column where they are contacted by chilled product (277K) drawn from product storage and absorbed. The fresh product stream is used first in the saturator, then it passes through an economizing heat exchanger as it enters the absorber. The rich absorbent also passes through the heat exchanger before being pumped back to storage. The operation of the control system is intermittent, starting when the vapor holder is filled and stopping when it has emptied or at its lower preset level. Cleaned gases are vented from the absorber column to the atmosphere.

A vapor recovery system employing a compression-refrigeration-condensation unit makes use of a vapor holder to store accumulated air-vapor mixture and a saturator for ensuring that the VOC concentration is above the explosive range. The unit is activated and begins processing vapors when the vapor holder has filled to a preset level. Incoming saturated air-vapor mixture is first compressed in a two-stage compressor with an intercooler. Condensate is withdrawn from the intercooler prior to compression in the second stage. The compressed vapors then pass through a refrigeration-condenser section where they are returned along with the intercooler condensate to a product storage tank. Cleaned gases are exhausted from the top of the condenser.

Costs for vapor processing units vary with the type of product and the product throughput. In the case of gasoline, capital investment costs for these units range from $152,000 to $270,000 for a gasoline throughput of 380 m^3/day. These costs increase by 15% when the gasoline throughput increases by 150% (91).

Costs for internal floaters range from approximately $4,000 to $40,000 for storage tanks with diameters of 5 and 30 m, respectively. Secondary seals are estimated to cost $75 per linear meter.

Fugitive Organic Emissions

There are many potential sources of fugitive organic emissions that result when process fluid (either liquid or gaseous) leaks from plant equipment in a typical gasification/liquefaction synthetic fuel plant. Some of these are: pumps, compressors, in-line process valves, pressure relief devices, open-ended valves, sampling connections, flanges, agitators, and cooling towers.

There are two basic methods which have been used to control fugitive organic emissions:

1) leak detection and repair methods and
2) equipment specification.

Leak detection methods include individual component surveys, area (walk-through) surveys, and fixed point monitors. In an individual component survey each fugitive emission source (pump, valve, compressor, etc.) is checked for VOC leakage. The source may be checked for leakage by visual, audible, olfactory, soap bubble, or instrument techniques. Visual methods are particularly effective in locating liquid leaks. Escaping vapors from high pressure leaks can be audibly detected, and leaks of odorous materials may be detected by smelling the odor. Perhaps the best method of identifying leaks of VOC from equipment components is by using portable detection instruments. By sampling and analyzing the air in close proximity to the leak, the hydrocarbon concentration of the sampled air can be determined. The leak rate from the source can be roughly estimated since relationships exist between monitoring concentrations and mass emission rates.

An area survey (also known as a walk-through survey) requires the use of a portable hydrocarbon detector and a strip chart recorder. The procedure involves carrying the instrument within one meter of the upwind and downwind sides of process equipment and associated fugitive emission sources. An increase in observed concentration indicates leaking fugitive emission sources. The instrument is then used for an individual component survey in the suspected leak area.

Fixed point monitors are automatic hydrocarbon sampling and analysis instruments positioned at various locations in the process unit. The instruments may sample the ambient air intermittently or continuously. Elevated hydrocarbon concentrations indicate a leaking component. As in the walk-through method, an individual component survey is required to identify the specific leaking component in the area. For this method, the portable hydrocarbon detector is also required.

Reduction of fugitive emissions from the identified leaking components is effected by repair methods. In many cases, perfect repair will not be achieved; however, effective repair can substantially reduce emissions from the leaking component. Typical repair methods employed on the various components are listed in Table 4-18.

TABLE 4-18. REPAIR METHODS FOR FUGITIVE EMISSIONS REDUCTION

Component	Repair Method
Pumps and compressors	Tighten packing gland
Relief valves	Manual release of the valve may improve the seat seal
In-line valves	Tighten packing gland Lubricate plug type valves Inject sealing fluid into process valves requiring repair
Flanges	Replace flange gaskets

The second method used to control fugitive emissions is by equipment specification. Typical equipment specifications used are listed in Table 4-19.

Costs for repair methods will depend upon the complexity of the component undergoing repair. The major costs of maintenance and repair methods are labor related. In the case of equipment specifications costs will depend upon the component being replaced. Typically, double mechanical seals cost $815/pump (installed). Flush oil systems for double mechanical seals cost $1500/pump.

TABLE 4-19. EQUIPMENT DESIGN/MODIFICATIONS FOR FUGITIVE HYDROCARBON EMISSIONS CONTROL

Pumps	- improve seal at the junction of moving shaft and stationary casing - use sealless pumps - use double mechanical seals - use closed vent systems around seal areas
Compressors	- improve seal at the junction of moving shaft and stationary casing - use double mechanical seals - use closed vent systems around seal areas
Pressure Relief Devices	- use rupture disks upstream from the safety/relief valve - use resilient seal or "o-ring" relief valves - use closed vent systems to transport valve discharge to control devices
Open-Ended Valves	- install a cap, plug, flange, or a second valve to the open end of the valve
In-Line Valves	- use diaphram and bellows seal type valves

4.1.5.1 Product/By-Product Storage Emissions

Various types of vessels are employed to store petrochemical products. The suitability of a specific tank design depends on the vapor pressure that the stored product exerts at ambient conditions and the type of storage desired. The floating roof tank is widely used for control of volatile organic compounds such as gasoline when the true vapor pressure is in the range of 10 to 80 kPa at storage conditions. Low vapor pressure VOCs (<10 kPa) are stored in fixed roof tanks. Therefore, it was assumed that methanol and gasoline products would be stored in floating roof tanks and diesel fuel and fuel oil in fixed roof tanks. Uncontrolled emissions estimates from these tanks have previously been discussed in Section 3.6.5.

Emissions from floating roof tanks consist primarily of standing storage losses and wetting losses. These losses are greatly reduced by the addition of secondary seals. The most widely used approach for VOC control is the addition of secondary seals to existing floating roof tanks. The secondary seal is generally of a resilient fabric (e.g., loop seals) or a pliable material such as a treated rubber. Its flexibility allows it to maintain contact in places where the shell might be slightly out of round as well as in areas where rivet heads project from the shell wall. Upon descent of the roof, these seals wipe down the film left behind by the primary seal. These seals also reduce standing storage evaporative losses since they form a second seal above the vaporized product which has diffused past (or permeated through) the primary seal. Not only do they form a second barrier for the vapor, they also seal this vapor off from the effects of moving air. As a result, secondary seals are effective control devices which, when used on floating roof tanks, can reduce overall emissions by as much as 98% (refer to Table 4-20).

Fixed roof tanks consist of a steel cylindrical shell with a permanently-affixed roof. The roof design may vary from cone-shaped to flat. Of presently employed tank designs, the fixed roof tank is the least expensive to

TABLE 4-20. STORAGE TANK EMISSION ESTIMATES

Product	Roof Type	Capacity (m^3)	Diameter (m)	Synthesis Case	Assumed Vapor Pressure (KPa)	Mass Emission Rate (kg/yr)*		Avg. Control Efficiency (%)
						Uncontrolled (kg/yr)	Controlled† (kg/yr)	
Methanol	Floating	3,200	18.2	Fischer-Tropsch	17.3	8,740	173	98.0
					8.83	6,630	125	98.1
Methanol	Floating	45,000	62.5	Methanol	17.3	59,790	1226	97.9
					8.83	45,360	896	98.0
Methanol	Floating	46,500	64	Mobil M	17.3	61,250	1256	97.9
					8.83	46,470	918	98.0
Gasoline	Floating	22,000	43.6	Fischer-Tropsch	49.78	21,790	1471	93.2
					33.85	20,430	1208	94.1
Gasoline	Floating	39,000	53.3	Mobil M	49.78	28,950	1955	93.2
					33.85	27,140	1605	94.1
Diesel	Fixed	3,600	19.5	Fischer-Tropsch	0.08	800	39.2	95.1
					0.046	500	38.8	92.2
Fuel Oil	Fixed	940	11.6	Fischer-Tropsch	0.00059	9	1.05	90
					0.0026	5	0.45	91

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*Calculations based on information contained in AP-42 (Reference 76). The higher values represent the month with maximum emissions (July). The lower number represents the average annual values. Location was assumed to be Southwest Illinois.

†Floating roof tanks were assumed to have both primary and secondary seals. Fixed roof tanks were assumed to have internal floaters with closure seals.

construct and is generally considered as the minimum acceptable standard for storage of petroleum liquids. Fixed roof tank emissions are most readily controlled by the installation of internal floating roofs. An internal floating roof tank is essentially a fixed roof tank with a cover floating on the liquid surface inside the tank which rises and falls with the liquid level. Calculations indicate that emission reductions of more than 90% are achieved by retrofitting fixed roof tanks with internal floating roofs. Other control technologies such as vapor processing systems can be also used to effect 90% control. However, internal floating roof covers are widely used because of their simplicity and their low annual operating and capital costs. Controlled emissions from fixed roof tanks are listed in Table 4-20.

Annual costs of applying secondary seals and internal floaters to storage tanks for the K-T based indirect liquefaction facility being discussed in this report are listed in Table 4-21. Secondary seals were assumed to cost \$130 per linear meter (92). The cost of the aluminum internal floating roof cover varies expotentially with the storage tank diameter and ranges from \$5500 for a 5m diameter tank to \$49,300 for a 30m diameter tank (92).

The capital investment and annualized costs for controls on fixed and floating roof tanks was estimated to be from \$25,500 to \$69,600 and \$5,900 to \$10,300, respectively. However, annualized costs are decreased considerably because of savings due to product recovered by use of these controls (refer to Table 4-21). These costs correspond to 0.002 to 0.005% of the base plant capital investment. The annualized costs are negligible when compared to base plant costs.

TABLE 4-21. ESTIMATED INCREMENTAL COSTS FOR STORAGE OF SYNTHETIC LIQUIDS*

Type of Liquid	Synthesis Case	Type of Control	Annualized Control System Costs	Annual Product Savings	Net Annual Cost	Controlled Emissions Costs $/kg/hr
Methanol ($3,200\ m^3$)	Fischer-Tropsch	Secondary seal	1,900	1,800	100	0.013
Methanol ($45,000\ m^3$)	Methanol	Secondary seal	5,900	12,100	(6200)†	0
Methanol ($46,500\ m^3$)	Mobil M	Secondary seal	6,000	12,300	(6300)†	0
Gasoline ($22,000\ m^3$)	Fischer-Tropsch	Secondary seal	4,200	7,000	(2800)†	0
Gasoline ($39,000\ m^3$)	Mobil M	Secondary seal	5,000	9,300	(4300)†	0
Diesel Oil ($3,600\ m^3$)	Fischer-Tropsch	Internal floater	5,200	150	5050	8.3
Fuel Oil ($940\ m^3$)	Fischer-Tropsch	Internal floater	3,500	1	3500	560

*250,000 kg/hr (MAF) coal feed to gasifier basis

†Parenthetic cost data represent credits

4.1.5.2 Fugitive Organic Emissions from Process Equipment (Stream 241)

As discussed earlier, process equipment such as pumps, compressors, in line valves, pressure relief devices, open-ended valves, etc., are prone to leakage and thus are sources of fugitive organic emissions. Two methods can be employed to control these emissions. A labor intensive method involving leak detection and constant repair and maintenance can be used, and/or replacement of leaking equipment by leak-free equipment. Obviously, if equipment specification in addition to extensive leak detection and repair is performed, greater reduction in fugitive organic emissions is achieved.

Two approaches to reduce fugitive organic emissions are generally used. In the first approach leak detection and repair methods (as suggested in the VOC leak control techniques guideline document for the petroleum industry) can be applied (93). Here, leak detection is accomplished by checking equipment components for emissions of VOC at specified intervals using a portable VOC detection instrument to sample and analyze the air in close proximity to the potential leak area. A measured VOC concentration greater than some predetermined level would indicate a leak that would require equipment repair. Inspection of all equipment has to be performed on a regular basis.

Controlled emission estimates for the K-T based indirect liquefaction facility under consideration were made assuming that the aforementioned approach was employed. Emission reductions of approximately 70% were estimated for the three synthesis cases as shown in Table 4-22. These estimates were based on a detection level of 10,000 ppm, weekly inspections of light liquid pump seals, monthly inspection of all other equipment, and open-ended valves were required to be sealed with a cap plug or another valve. Capital investment and annualized costs were estimated to range from $41,000 to $145,000 and $251,000 to $102,000, respectively (refer to Table 4-23). These

TABLE 4-22. FUGITIVE ORGANIC EMISSIONS FROM PROCESS EQUIPMENT

	Uncontrolled Emission Factor† (kg/hr)	Uncontrolled Emission Rates (kg/hr)			Controlled Emission Rates (kg/hr)		
		Fischer-Tropsch	Methanol	Mobil M	Fischer-Tropsch	Methanol	Mobil M
Pump Seals*							
Light Liquid Service	0.154	16.74	3.17	7.09	0 - 4.19	0 - 0.79	0 - 1.77
Heavy Liquid Service	0.029	0.52	0.23	0.38	0 - 0.44	0 - 0.19	0 - 0.32
In-Line Valves							
Gas Service	0.027	34.72	7.78	15.39	3.47	0.78	1.54
Light Liquid Service	0.011	37.02	7.09	15.68	9.63	1.84	4.08
Heavy Liquid Service	0.00023	0.14	0.06	0.09	0.14	0.06	0.09
Safety Relief Valves							
Vapor Service	0.086	24.77	5.16	11.35	9.41	1.96	4.31
Compressor Seals*							
Hydrocarbon	1.28	12.8	2.88	1.54	0 - 3.84	0 - 0.86	0 - 0.46
Hydrogen	0.10	1.8	--	--	0 - 0.86	--	--
Flanges	0.00025	1.09	1.18	2.42	1.09	1.18	2.42
Drains	0.07	10.94	2.45	4.90	6.35	1.42	2.84
Totals		140.5	30.0	58.8	30.1 - 39.4	7.2 - 9.1	15.3 - 17.8

*Uncontrolled emission factors for pumps and compressors represent emissions from each pump and compressor and not from each pump seal and compressor seal.

†These factors are averages for all sizes of the items indicated. Data are not sufficient at present to allow emission rates to be related to equipment sizes.

costs correspond to 0.004 to 0.011% of the base plant capital investment and 0.007 to 0.025% of the base plant annualized costs.

The second approach goes a step beyond the first in that it relies on equipment specification in addition to leak detection, repair, and maintenance. Monitoring requirements are similar to those for the first approach except in cases where equipment specification eliminates the need for monitoring. Typical equipment specifications can consist of caps for open-ended valves, rupture disks on gas service relief valves, and double mechanical seals with a seal oil flushing system on pumps. In addition, compressor seal areas and degassing vents from oil reservoirs seals can be connected to a control device with a closed vent system. As a result of these equipment specifications, fugitive emissions from pumps, safety/relief valves, compressors, and sampling connections can be completely controlled.

On applying these specifications to the K-T based indirect liquefaction facility, an emission reduction of approximately 80% can be achieved. The capital investment and annualized costs for these controls are estimated to be from \$0.3 million to \$1.9 million and \$0.09 million to \$0.75 million, respectively, as listed in Table 4-23. These costs correspond to 0.03 to 0.14% of the base plant capital investment and 0.03 to 0.19% of the annualized base plant cost.

TABLE 4-23. CAPITAL AND ANNUALIZED COSTS FOR FUGITIVE ORGANIC EMISSION CONTROLS

	Fischer-Tropsch		Methanol		Mobil M	
Cost Item	Leak Detection, Repair, and Maintenance	Equipment Specification	Leak Detection, Repair, and Maintenance	Equipment Specification	Leak Detection, Repair, and Maintenance	Equipment Specification
Capital Cost ($)	145,000	1,876,300	41,400	311,900	69,700	531,400
Annualized Cost ($)	102,200	754,200	24,900	93,900	43,600	178,000

TABLE 4-23. CAPITAL AND ANNUALIZED COSTS FOR FUGITIVE ORGANIC EMISSION CONTROLS

	Fischer-Tropsch		Methanol		Mobil M	
Cost Item	Leak Detection, Repair, and Maintenance	Equipment Specification	Leak Detection, Repair, and Maintenance	Equipment Specification	Leak Detection, Repair, and Maintenance	Equipment Specification
Capital Cost ($)	145,000	1,876,300	41,400	311,900	69,700	531,400
Annualized Cost ($)	102,200	754,200	24,900	93,900	43,600	178,000

4.1.6 Fugitive Particulates from Material Conveying and Processing

Material transfer and conveying operations are common to nearly all processing industries. Equipment includes belt conveyors, screw conveyors, bucket elevators, vibrating conveyors, and pneumatic conveyors. The type of conveying equipment varies with the application and is determined primarily by the quantity and characteristics (size, specific gravity, moisture content, etc.) of the material being handled, the transfer distance and elevation, and the working conditions. Loss of material from conveyors occurs primarily at the feeding, transfer, and discharge points due to spillage or wind. The majority of particulate emissions are generally from spillage and mechanical agitation of the material at transfer points.

Material from storage piles is generally crushed, screened, and pulverized prior to transfer to the boiler or gasification plants. Fugitive dust generated during this process is typically controlled by either wet suppression techniques or dry particulate collection systems.

Fugitive particulate control systems utilizing a wetting agent consist of pre-engineered modules which incorporate both water handling components and automatic spray controls. A typical spray solution contains 1,000 to 4,000 parts of water to one part of a wetting agent. The rate of spray application is about 4 to 8 liters/Mg of material. This rate of application results in an increase of total surface moisture by about 0.5 to 1.0%.

In wet dust suppression, the fugitive particulates are first confined by a curtain of moisture droplets. Then the wetting of dust takes place by contact and penetration with moisture droplets. Finally, agglomerates are formed by contact with other droplets and settling takes place because of the additional weight of the other droplets. Wet suppression techniques can cost from $0.33 to $0.77/Mg of material treated depending upon the wetting agent utilized.

Dry particulate collection systems consist of enclosures to contain the particulates, ductwork and exhaust systems to convey the particulate laden air, and particulate collectors to separate the particulate from the air. Typically, hoods are used to capture particulate emissions at transfer points. Conveyors generally have a half cover which provides dust containment and also shields the conveyor from wind, rain, and snow. The type and size of enclosure depends upon the particulate source. Data on ductwork velocities needed for particulate capture for different source types are readily available (94). Dust collectors that are applicable to the collection of the captured particulate are: (1) venturi scrubbers, (2) electrostatic precipitators, (3) fabric filters, and (4) dry centrifugal collectors. These have been discussed previously in Section 4.1.2.

4.2 AQUEOUS MEDIUM

A variety of wastewater streams are generated by a K-T gasification facility. Individual streams and their characteristics are summarized in Table 4-24. The shift condensate (Stream 218) and methanation condensate (Stream 236) contain only carbon dioxide and, therefore, probably require little or no treatment prior to being recycled to the plant as makeup water or otherwise handled. These two streams are not considered in this section. All other wastewater streams are classified in Table 4-25 as either streams of an inorganic or organic source type. The inorganic streams are further identified according to the predominating species present: reduced volatile, reduced nonvolatile, and oxidized inorganics.

This section considers the control of only those wastewater streams that significantly influence the wastewater treatment approach required for the entire K-T gasification facility. In Section 4.2.1, a summary of control technologies potentially applicable to these wastewater streams is presented. In Section 4.2.2 and 4.2.3, performances of individual controls applied to specific wastewater streams of either the organic or inorganic source type are discussed.

The overall control of wastewater streams generated by a K-T gasification facility generally involves more than one control process applied to either an individual stream or to a composite of several streams. Performance and costs of individual controls are most meaningfully assessed in the context of integrated trains, but exact definition of these integrated trains can be made only when data specific to a particular facility are available. However, certain combinations of controls are believed to be likely, and integrated control examples are therefore presented in Section 4.2.4 along with corresponding performances and costs. These combinations are intended as examples only and are not to be construed as EPA recommendations.

TABLE 4-24. SUMMARY OF K-T BASE PLANT WASTEWATER STREAMS AND ESTIMATED CHARACTERISTICS

Characteristic*	Flow[†] m^3/hr	Cl^-	CN^-	SCN^-	$S^=$	$S_2O_3^=/SO_3^=$	NH_3	TDS[#]	COD	TOD	TSS	Trace Elements
Wastewater Streams from Coal Preparation												
ROM Coal Storage Pile Runoff (Stream 201)												
- Methanol Synthesis	151	-[§]	-	-	-	-	-	-	-	-	Present[‡]	Present
- Mobil M Synthesis	146	-	-	-	-	-	-	-	-	-	Present	Present
- Fisher-Tropsch Synthesis	174	-	-	-	-	-	-	-	-	-	Present	Present
Wastewater Streams from Gas Purification and Upgrading												
Gas Cooling/Dust Removal Blowdown (Stream 210)	322	2111	7	4	1	128	156	4000	113	4	Present	Present
Raw Gas Compression and Cooling Condensate (Stream 211)	17.4	2200	8.9	14	48.7	6.3	735	-	124	7	-	-
Cyanide Wash Water (Stream 215)	239	-	241	Present	176	-	-	-	500	111	-	-
Cyanide Wash Still Bottoms (Stream 213)	0.001	-	10	Present	-	-	-	-	6	5	-	-
Shift Condensate (Stream 218)	180	-	-	-	-	-	-	-	-	-	-	-
Rectisol Condensate/ Still Bottoms (Stream 220)	1.2	-	10	-	-	-	-	-	6	5	-	-

(Continued)

TABLE 4-24. (Continued)

Characteristic*	Flow† m^3/hr	Cl^-	CN^-	SCN^-	$S^=$	$S_2O_3^=/SO_3^=$	NH_3	TDS#	COD	TOC	TSS	Trace Elements
Wastewater Streams from Synthesis of Liquid Fuels												
Methanol Distillation Condensate (Stream 229)	10	-	-	-	-	-	-	-	33000	4400	-	-
F-T Wastewater (Stream 223)	160	-	-	-	-	-	-	Present	12000	4300	Present	-
Mobil M Wastewater (Stream 233)	110	-	-	-	-	-	-	-	14000	4000	-	-
Methanation Condensate (Stream 236)	12.9	-	-	-	-	-	-	-	-	-	-	-
Wastewater Streams from Additional												
Demineralizer Regeneration Wastewater (Stream 301)	18	167	-	-	-	-	-	7200	-	-	-	-
Boiler Blowdown (Stream 303)	2.1	-	-	-	-	-	-	400	Present	Present	Present	Present
Cooling Tower Blowdown (Stream 307)												
- Methanol Synthesis	161	-	-	-	-	-	-	-	-	-	-	Present
- Mobil M Synthesis	180	-	-	-	-	-	-	-	-	-	-	Present
- F-T Synthesis	236	-	-	-	-	-	-	-	-	-	-	Present

(Continued)

TABLE 4-24. (Continued)

Characteristic[*]	Flow[†] m^3/hr	Cl^-	CN^-	SCN^-	$S^=$	$S_2O_3^=/SO_3^=$	NH_3	TDS[#]	COD	TOC	TSS	Trace Elements
Miscellaneous Waste Streams												
Process Equipment Cleaning Wastes (Stream 242)	-	-	-	-	-	-	-	Present	Present	Present	Present	Present
Boiler Cleaning Wastes (Stream 305)	-	-	-	-	-	-	-	Present	Present	Present	Present	Present
Storm Runoff (Stream 314)	47	-	-	-	-	-	-	-	Present	Present	Present	Present
Plant Process Drain (Stream 315)	32-42	-	-	-	-	-	-	-	Present	Present	Present	Present
Wastewater Streams from Air Pollution Control Processes												
Wellman-Lord Condensate (Stream 411)	3	-	-	-	-	Present	-	Present	Present	-	-	Present
Beavon Condensate (Stream 405)	4	-	-	-	Present	-	Present	-	Present	-	-	-
SCOT Condensate (Stream 409)	4	-	-	-	Present	-	Present	-	Present	-	-	-
Stretford Solution Purge (Stream 405)	2-3	-	-	Present	-	Present	-	Present	Present	-	-	Present
Flue Gas Desulfurization Purge (Stream 425)												
- Mobil M case	6.1	-	-	-	-	Present	-	Present	Present	-	Present	Present
- F-T case	37.5	-	-	-	-	Present	-	Present	Present	-	Present	Present

[*] All concentrations are mg/L.

[†] For a plant with an input to the gasifier of 278 mg/hr of dry Illinois No. 6 coal.

[‡] Present but not readily quantified.

[§] A dash indicates that this is not an important constituent/parameter in this stream.

[#] TDS is Total Dissolved Solids; COD is Chemical Oxygen Demand; TOC is Total Organic Carbon; TSS is Total Suspended Solids.

TABLE 4-25. CATEGORIZATION OF AQUEOUS WASTE STREAMS IN K-T GASIFICATION FACILITIES

Source Type	Stream Name	Factors Affecting Flow Rate and Pollutant Loading
Inorganic-predominantly reduced nonvolatiles	Gas cooling/dust removal blowdown (Stream 210)	Species other than NH_3 are believed to be generally independent of coal type. Ammonia production generally increases with decreasing coal rank. TDS and Cl^- levels in the circulating wash water determine the blowdown flow and these constituents are related to the Cl^- and ash content of the coal.
	Wellman-Lord condensate (Claus tail gas treatment) (Stream 411)	Flow is design specific but not necessarily related to coal rank. Loading is related to coal sulfur content.
	Stretford solution purge (Stream 405)	Flow and loading are related to coal sulfur content.
	Flue gas desulfurization purge (Stream 425)	Flow and loading are related to coal sulfur content and boiler size.
Inorganic-predominantly reduced volatiles	Cyanide wash water (Stream 215)	Flow and loading are qualitatively similar for most coal types.
	Compression condensate (Stream 211)	Flow and loading are qualitatively similar for most coal types.
	Beavon condensate (Stream 405)	Flow is design specific but not necessarily related to coal rank. Loading is related to coal sulfur content.
	SCOT condensate (Stream 409)	Flow is design specific but not necessarily related to coal rank. Loading is related to coal sulfur content.

(Continued)

TABLE 4-25 (Continued)

Source Type	Stream Name	Factors Affecting Flow Rate and Pollutant Loading
Inorganic-predominantly oxidized species	Cooling tower blowdown (Stream 307)	Cooling tower blowdown is not dependent on coal type. Flow and loading are related to the makeup water quality, the amount of wet versus dry cooling in the base plant, the climatic conditions at the facility, cycles of concentration, and quantity of inhibitory chemicals added.
	Coal storage pile runoff (Stream 201)	Coal type and conditions of wastewater contact with coal (e.g., residence time and temperature). Rainfall rates, coal storage, and washing practices.
	Demineralizer regeneration wastewater (Stream 301)	Makeup water flow and characteristics.
	Boiler blowdown (Stream 303)	Size of the boiler and boiler operating pressure.
	Boiler cleaning wastes (Stream 305)	Plant operating, maintenance, and boiler cleaning practices; boiler size.
Organic	F-T synthesis condensate (Stream 223) Mobil M synthesis condensate (Stream 233)	Flow and loading are independent of coal type fed to the gasifier. Type of organics depend on the operating conditions and by product recovery.
	Methanol distillation wastewater (Stream 229)	Flow and loading are independent of coal type. Flow depends on CO_2 in the synthesis gas.

(Continued)

TABLE 4-25 (Continued)

Source Type	Stream Name	Factors Affecting Flow Rate and Pollutant Loading
Organic (continued)	Rectisol still bottoms (Stream 220)	Flow and loading are not specific to coal type.
	Cyanide wash still bottoms (Stream 213)	Flow and loading are not specific to coal type.
	Process equipment cleaning wastes (Stream 242)	Waste stream source; plant operating, maintenance and equipment cleaning practices.
	Storm runoff (Stream 314)	Climatic conditions; housekeeping and maintenance practices.
	Plant process drain (Stream 315)	Total plant water makeup; housekeeping and maintenance practices.

The following wastewater streams are believed to most directly influence the overall wastewater treatment approach taken at a K-T gasification facility: the gas cooling/dust removal blowdown (Stream 210) of the reduced nonvolatile inorganics source type; the cyanide wash water (Stream 215) and the compression condensate (Stream 211) of the reduced volatile inorganics source type; and the three synthesis condensates (F-T, Stream 223; Mobil M, Stream 233; and methanol distillation, Stream 229) of the organic source types. The waste streams containing primarily inorganic contaminants (Streams 210, 211, and 215) are generally considered unique to K-T indirect liquefaction facilities. Streams similar to the synthesis condensates (Streams 223, 229, and 233) would be generated regardless of the type of gasifier employed. The gas cooling/dust removal blowdown is a major source of wastewater flow and contains significant concentrations of ammonia, chloride, TDS, and reduced sulfur species other than sulfide. For base plant designs where cyanide is removed in the gas upgrading section by a water-based wash (see Section 3.3.4), the cyanide wash water is another major source of wastewater flow. This stream contains most of the cyanide that was originally in the gasifier offgas and sulfide. Condensate from the raw gas compression and cooling circuit is a low flow stream but contains significant loadings of ammonia, chloride, and cyanides. The methanol distillation condensate and the F-T and Mobil M synthesis condensates contain varying loads of organics, typically ketones, organic acids, and/or methanol.

All other wastewater streams generated by the K-T gasification facility should not influence the overall wastewater treatment approach. Each would be routed to existing controls designed for other, more heavily loaded wastewater streams. These streams would contribute only a small fraction of the total load and flow such that the performance and economics of individual controls would be affected only slightly.

The remaining wastewater streams probably do not influence the facility-wide wastewater treatment approach, and are generally not unique to K-T gasification facilities. These streams include the Beavon (Stream 405) and SCOT (Stream 409) condensates of the reduced volatile inorganics source type; the Wellman-Lord condensate (Stream 411), Stretford solution purge (Stream 405), and flue gas desulfurization purge (Stream 425) of the reduced nonvolatile inorganics source type; the cooling tower blowdown (Stream 307), ROM coal storage pile runoff (Stream 201), demineralizer regeneration wastewater (Stream 301), boiler blowdown (Stream 303), and boiler cleaning wastes (Stream 305) of the oxidized inorganics source type; and the process equipment cleaning wastes (Stream 242), storm runoff (Stream 314), and plant process drain (Stream 315) of the organic source type. Certain of these streams have small flows/loadings and would be routed to existing controls designed for larger wastewater streams with no significant effect on the performance or economics of the control. Others, such as the ROM coal storage pile runoff or the cooling tower blowdown, have large flows/loadings but have characteristics that are not amenable to treatment by the controls for other streams. Streams of this type would probably be handled by separate controls. None of these streams are unique to K-T gasification facilities, and their control has been well developed in parallel industries, particularly petroleum refining and electric utilities.

4.2.1 Water Pollution Control Processes

This section presents general information for a variety of water pollution control processes which are potentially applicable to the treatment, disposal, and/or reuse of wastewaters from K-T-based gasification plants. The information presented in this section is derived from industrial applications and laboratory tests with various wastewaters. The water pollution control technologies discussed do not represent an all-inclusive list of processes, as others may be available or may be developed. Rather, these processes represent control alternatives which have been commercially applied in analogous applications or have potential for commercial application. Table 4-26 lists the treatment processes which are potentially applicable to wastewaters from the K-T facility and presents summary information about each. This section expands on the summary information for some of the controls.

The water pollution control processes discussed include techniques for:

- removal of suspended solids, tars, and oils;
- removal of bulk organics;
- removal of dissolved gases;
- removal of dissolved inorganics;
- removal of dissolved organics;
- removal of residual organics;
- volume reduction; and
- residual disposal.

A more detailed discussion of each may be found in the Control Technology Appendices.

TABLE 4-26. CONTROL PROCESSES POTENTIALLY APPLICABLE TO THE TREATMENT OF K-T-BASED GASIFICATION PLANT WASTEWATERS

Technology	Technology Principle	Components Removed	Removal Efficiency	Feed Requirements/ Restrictions	By-Products and Secondary Waste Streams	Estimated Capital Cost	Comments
Removal of Suspended Solids, Tars, and Oils							
Gravity separation - API oil separator - parallel plate	Provision of adequate residence time in a stagnant vessel to allow suspended solids or immiscible fluids to separate into lighter and heavier than water phases	Suspended solids, tars, and oils	Depends upon design, 10-50% removal of TSS typical, 60-99% for oils	Minimum feed stream turbulence	Recovered oils (Sp. gr. <1), sludges/solids (Sp. gr. >1)	--	Incorporated into the tar/oil separation system design in all existing Lurgi gasification plants.
Coagulation/ flocculation	Use of agents to promote the coalescence of fine suspended solids and adsorption of tars and oils; generally used in conjunction with a gravity separation process	Promotes removal of finely dispersed particles	Outlet suspended solids concentration to 10 mg/L possible, oils removal of 60-95%	A wide range of commercial flocculants are available	Same as gravity separation	--	Widely used in water treatment system to remove fine solids.
Air flotation - dissolved air - induced air	Use of air bubbles to promote the disengagement of lighter-than-water materials from solution	Suspended oils and solids	Depends on characteristics of source and treatment process; TSS removal of 20-75%, oil removals of 75-85%	Air requirements depend upon waste characteristics	Recovered oils, entrained solids	--	Of limited usefulness in treating gasification plant wastewaters
Filtration	Passing wastewater through suitable filter medium; filter material discarded or cleaned by backflushing	Depends on filter medium; both coarse and fine structure materials are used industrially	TSS removals of 30-90+%, oil removals of 65-90%	Filter media	Filter backwash; spent filter media	$1700 per m^3/hr	Proposed for use as polishing step for phenolic water downstream of tar/oil separation; "Sticky" tars/oils may cause problems with filter plugging and regeneration.
Removal of Bulk Organics							
Solvent extraction - Phenosolvan - Chem-Pro	Extraction of organics from wastewater via contact with an immiscible solvent. Byproduct organic liquids recovered from the solvent in a separate regeneration step.	Phenols, TOC, BOD, COD, other organics	Phenosolvan: - monohydric phenol 99.5% - polyhydric phenol 60% - organic acids 15% Chem-Pro: - monohydric phenol 99.8% - dihydric phenol 95% - trihydric phenol 90-95% - other organics 50+%	Sensitive to suspended matter is wastewater, makeup solvent	Crude phenols, filter backwash, spent filter media	--	Phenosolvan is the process used in all major Lurgi facilities. Chem-Pro process is commercially applied in phenol formaldehyde resin manufacturing plants. First application in 1961 to recover phenol from coke-oven waste liquor.

(Continued)

TABLE 4-26 (Continued)

Technology	Technology Principle	Components Removed	Removal Efficiency	Feed Requirements/ Restrictions	By-Products and Secondary Waste Streams	Estimated Capital Cost	Comments
Wet air oxidation	Direct reaction of O_2 with wastewater in a closed, pressurized vessel at elevated temperatures	Same as biological oxidation except better destruction of cyanides and other difficult to treat organics can be achieved	90+% removal of COD is possible in a system with a residence time of 1 hour or greater	Air or oxygen; heat if autothermic reaction conditions are not present	Vent gases containing CO, CO_2, light hydrocarbons, NH_3, sulfur species	--	Promising but not proven in this application; fairly rigorous materials of construction requirements.
Removal of Dissolved Gases							
Steam stripping	Increasing temperature and providing a positive flow of inert material (steam) through the wastewater; removes volatile organics and inorganics with overhead steam	NH_3, acid gases (CO_2, H_2S, HCN), light hydrocarbons (phenols)	95-99% removal of "free" ammonia and acid gases typical; hydrocarbon removal varies with volatility of stripped components	Feed preheat can be used to reduce steam requirements; acid/caustic for pH adjustment optional	Stripped gases, uncondensed steam	--	Acid/caustic addition can be used to improve the efficiency of the stripping process.
- Phosam-W			Removal to: 150 mg/L NH_3 1 mg/L H_2S, CO_2. 95% HCN removal				
- Chevron WWT			Removal to: 50 mg/L NH_3 5 mg/L H_2S				
Inert gas stripping	Same as with steam except that an inert gas such as N_2, air or CO_2 is used as the stripping medium	Same as for steam stripping	Same as for steam	Generally operates at lower temperature than steam stripping process	Stripped gases, stripping gas	--	The presence of an inert stripping gas as a diluent may make it more difficult to handle or further treat the gases stripped from the wastewater.
Vacuum distillation	Low pressure, low temperature stripping process	Same as for steam stripping	Same as for steam	Same as for inert gas stripping	Stripped gases	--	High energy requirements; not cost competitive in a plant where stripping steam is readily available.
Selective absorption	Used in conjunction with one of the above processes to selectively absorb stripped gases	NH_3 (with acidic solutions), acid gases (with basic solutions)	90+% removal of acid gases or NH_3 is typical	Makeup acid/ caustic	Recovered NH_3 or acid gases, rich sorbent	--	This is the basis for several commercially proven processes for recovering high purity ammonia.

(Continued)

TABLE 4-26 (Continued)

Technology	Technology Principle	Components Removed	Removal Efficiency	Feed Requirements/ Restrictions	By-Products and Secondary Waste Streams	Estimated Capital Cost	Comments
Removal of Dissolved Inorganics							
Ion exchange	Substitution of H^+ Na^+, OH^-, or Cl^- ions for other ionic species, exchange resins regenerated with acid, base, or salt solutions	Heavy metal, F^-, CN^-, scaling species, NH_3	90^+% removal for most ions, regeneration frequency is a key parameter	Regenerants, replacement resins	Spent regenerants and resins, treated water	\$5700 per kg NH_3-N per day	Most effective as a polishing process. Clearly applicable to boiler feedwater treatment needs. Of limited use in treating process watewaters containing high concentrations of organics or dissolved solids
Chemical precipitation	Use of agents to promote the precipitation of inorganic solids from wastewaters	Ca, Mg, heavy metals, alkalinity	Varies with waste stream constituents. Typical removals: Cd 2% Ni 50% Cr 40% Pb 5% Cu 20% Se 10% Hg 20% Zn 25%	Lime, polymer, and soda ash may be required.	Sludge contaminated with heavy metals	--	Generally followed by filtration and/or activated carbon adsorption.
Polysulfide addition	Cyanide converted to thiocyanate by polysulfide	CN^-	Varies	Possible chemical requirements for pH control.	Residual polysulfide; increased NH_3 concentration due to NH_4^+ as counter ion to polysulfide	\$530 per m^3/hr	This process utilized at petroleum refineries to control cyanide-induced scaling. No experience exists at the wastewater treatment process level.
Activated sludge	Microorganisms mediate oxidation of ammonia and thiocyanate	NH_3, SCN^-	90^+% for NH_3, SCN^-	Air or oxygen, supplemental nutrients may be required; relatively constant feed temperature and pollutant loadings required.	Biological oxidation sludge	\$4400 per equivalent kg NH_3-N per day	Used extensively to treat wastewaters of a wide range of characteristics and sources.
Biological denitrification	Microorganisms reduce nitrate to molecular nitrogen in the process of oxidizing methanol or some other organic	NO_3^-	90^+%	Nutrients; constant loading conditions	Biological oxidation sludge	\$2300 per kgN per day	Experience exists in both municipal and industrial applications.

See also: chemical oxidation, membrane separation, and forced evaporation.

(Continued)

TABLE 4-26. (Continued)

Technology	Technology Principle	Components Removed	Removal Efficiency	Feed Requirements/ Restrictions	By-Products and Secondary Waste Streams	Estimated Capital Cost	Comments
Removal of Dissolved Organics							
Biological oxidation - act. sludge - trickling filter - rotating biological contactor - lagoons - high purity oxygen (HPSAS)	Biological conversion of the carbonaceous organic matter in wastewater to cell tissue and various gaseous end products.	TOC, BOD, COD, some inorganic pollutants	Varies with waste stream characteristics. Typical removals: BOD 60-90% COD, TOC 80% total phenol 95% org acids 95% oil & grease 70% CN^- 70%	Air or oxygen, supplemental nutrients may be required; relatively constant feed temperature and pollutant loadings required to minimize "shocks" to system	Biological oxidation sludge	Activated sludge: $700 per kg BOD per day	This is the basis for the treatment of coke oven wastewaters
Wet air oxidation	Direct reaction of O_2 with wastewater in a closed, pressurized vessel at elevated temperatures	Same as biological oxidation except better destruction of cyanides and other difficult to treat organics can be achieved	Over 90% removal of COD is possible in a system with a residence time of 1 hour or greater. Actual efficiency heavily dependent upon waste characteristics.	Air or oxygen; heat if autothermic reaction conditions are not present	Vent gases containing CO, CO_2, light hydrocarbons, NH_3, sulfur species	--	Promising but not proven in this application; fairly rigorous materials of construction requirements.
Ultrafiltration	Forcing wastewater through semipermeable membrane under pressure	Most effective with high molecular weight organics	Up to 95% removal for total organics	Filter media	Spent filter media; concentrated wastewater	--	May be attractive as a preconcentration step prior to wastewater incineration.
Anaerobic digestion	Reduction of organics in closed vessel at moderate temperatures to form CH_4 and other hydrocarbons, digestion process relies upon metabolic processes of anaerobic organisms	TOC, BOD, COD	Unknown - this process has not been applied to these types of waste streams	Some supplemental nutrients may be required	Waste gases (combustible)	--	Kinetic limitations and process control problems could be substantial.

(Continued)

TABLE 4-26 (Continued)

Technology	Technology Principle	Components Removed	Removal Efficiency	Feed Requirements/ Restrictions	By-Products and Secondary Waste Streams	Estimated Capital Cost	Comments
Removal of Residual Organics							
Activated carbon adsorption	Adsorption of organics in water by activated carbon or polymeric resin, powdered activated carbon has been used in conjunction with biological processes (above) with some success in the organic chemical industry	Most effective with phenols; some heavy metal removal expected	Varies with waste stream characteristics. Typical removals: BOD 60% COD 80% TOC 70% Phenols 99.9% org acids 70% CN⁻ 50% SCN⁻ 50% tars 99% oils 99%	Low TSS, pH 6-9; high TOC loadings are less amenable to treatment.	Spent adsorbent regeneration off-gases	$260 per kg COD per day	Probably more effective as a polishing rather than a bulk organics removal process.
Chemical oxidation	Reaction of organics in wastewater with ozone, peroxides or chlorine-based oxidants	TOC, BOD, COD, oxidizable inorganics	High removals achievable depending upon conditions of operation	Oxident	Vent gases, wastewater, and reaction products	$850 per m^3/hr (Cl_2 and lime basis)	Chlorine-based oxidants may cause problems with treated wastewater.
Thermal oxidation (Incineration)	Combustion of organics	All oxidizable organics	Essentially complete destruction of organics in properly designed system	Supplemental fuel, preconcentration will improve performance and lower supplemental fuel requirements	Flue gases	$300,000 per m^3/hr	This will be the most effective process for removing organics but the supplemental fuel requirements may be substantial.
Cooling tower oxidation	air oxidation (and stripping) of organics and dissolved gases	TOC, COD, BOD, phenols and other organics, NH_3	Unknown - this process has been tested using SASOL wastewaters on a pilot scale but results are not available	Sensitive to suspended matter, oils, high TDS	Blowdown/drift		Treated wastewater use in small refinery cooling towers has be practiced - 75-80% reduction in wastewater volume is common.
Volume Reduction							
Membrane separation - reverse osmosis	Use of semipermeable membrane and pressure to separate water from its dissolved constituents	Relative rejection efficiencies of the various soluble species will be determined by membrane characteristics and conditions of process operation	90-95% rejection of dissolved salts. Reductions in dissolved organics and BOD of up to 99%	Membrane	Spent membrane material, recovered water, brine	--	May be useful as preconcentration step prior to further treatment or ultimate disposal of wastewater. Membrane scaling and fouling with organics may limit the applicability of this technology to the treatment of process condensates.
- electrodialysis	Use of selective anion- or cation-permeable membranes with electric field to separate mineral ions from water						

(Continued)

TABLE 4-26 (Continued)

Technology	Technology Principle	Components Removed	Removal Efficiency	Feed Requirements/ Restrictions	By-Products and Secondary Waste Streams	Estimated Capital Cost	Comments
Forced evaporation	Thermally induced evaporation of excess wastewater, condensate recovery optional	All nonvolatile species will remain in brine		None	Recovered condensate, noncondensible gases, waste brine	\$86,000 per m^3/hr feed	Very stringent materials requirements due to potential corrosion. Forced evaporation is energy intensive.
Cooling tower concentration	Wastewater used as partial makeup to the cooling tower and thereby concentrated into the blowdown.	All nonvolatile species concentrated into the blowdown		Feed characteristics limited by corrosion, scaling, and biological fouling	Evaporation/ drift		
Residual Disposal							
Deep well injection	Wastes are pumped into subsurface geological formations where they are isolated from all surface and groundwater supplies	Entire stream	100%	Injected fluids must be filtered to 5 micrometers and have a low organic content to prevent plugging. Wastes must not precipitate in the well or when mixed with subsurface fluids. Volume reduction prior to injection is often economical.	None	\$160,000 per m^3/hr	Applicability highly site specific.
Surface impoundment	Wastes are held in a containment basin	All nonvolatile species remain as residual in the impoundment	100%	Concentrations of volatile species may need to be low to prevent loss to the atmosphere	Loss of volatile species	\$52,000 per m^3/hr	Possibly large land requirements may limit applicability.
Co-disposal	Ash is quenched with wastewater then handled by a solid waste disposal technique	Entire stream	100%	Concentrations of volatile species may need to be low to prevent loss to the atmosphere	Loss of volatile species		Presence of certain chemical species in the quench water may yield an ash that requires handling as a hazardous material.
Surface discharge	Wastes are conveyed to and mixed with a natural water source	Entire stream	100%	Restrictions are site-specific	None		Assimilative capacity of receiving body must be investigated.

4.2.1.1 Processes for Removal of Suspended Solids, Tars, and Oils

A variety of control processes have been summarized in Table 4-26 that are applicable to waste streams having high concentrations of suspended solids, tars, and/or oils. The process or combination of processes selected for a particular waste stream would depend on the concentration of the contaminant species and its physical properties such as size distribution, specific gravity, and surface properties. This section summarizes available information for filtration as an example of a control process for removal of suspended solids, tars, and oils..

Filtration is a well-established technology that finds nearly industry-wide application. The process consists of passing a waste stream by either gravity or pressure through a bed of inert material which physically retains the solids suspended in the flow. Various materials and combination of materials have been used for filter media including sand, anthracite, activated carbon, natural/synthetic fibers, resins, and garnet. Performance varies with different media materials, and the material giving optimal performance must generally be determined by direct testing of the subject waste streams.

During the course of filtration, the bed becomes increasingly loaded with suspended solids resulting in a corresponding increase in the hydraulic headloss. At some point, the bed must be backwashed to return it to a condition approximating its original, unused state. About 2 to 10% of the filter throughput is needed for backwash, and this amount is stored during the filter run. Thus, suspended material contained in the waste stream is concentrated by a factor of 10 to 50.

Suspended solids removal by filtration typically range from 30 to 70 percent. Exact performance can be determined only by testing the waste stream to be treated.

4.2.1.2 Processes for Removal of Bulk Organics

For waste streams having high organic loadings, it is sometimes advantageous to apply a process capable of achieving gross organic removal. These processes can typically achieve high percentage removals, but since the feed stream is heavily loaded, an appreciable concentration of the contaminant species remains in the effluent. Other processes that are capable of reducing the contaminants to the low levels possibly required for ultimate disposal can follow these, if desired.

Processes for removal of bulk organics are presented in Table 4-26. These processes are not expected to be generally applied to any of the wastewater streams generated by a K-T gasification facility.

4.2.1.3 Processes for Removal of Dissolved Gases

Dissolved gases such as HCN, H_2S, and NH_3 can be removed from wastewaters by several processes. Some of these processes are summarized in Table 4-26. Most are designed to handle waste streams having high loadings of dissolved gases. High percentage reductions are possible in such cases, but the concentration of dissolved gas remaining typically requires additional controls of the waste stream. Residual levels achievable with techniques such as steam or inert gas stripping are similar to those already found in K-T gasification wastewaters (except cyanide wash water).

In the case of cyanide wash water (Stream 215) which is expected to contain several hundred ppm each of HCN and H_2S, stripping with inert gas may be applicable. Potential stripping gases which would probably be available onsite include waste nitrogen from an air separation plant or waste CO_2 from a selective Rectisol unit. The HCN laden offgas could be incinerated or sent to a Claus plant for treatment.

4.2.1.4 Processes for Removal of Dissolved Inorganics

A variety of processes summarized in Table 4-26 are applicable to waste streams requiring removal of dissolved inorganics. Processes such as chemical precipitation, membrane separation, and chemical oxidation are capable of removing simultaneously a wide variety of inorganic species. Others are narrowly applicable to one or a few specific species. These processes include ion exchange using a clinoptilolite resin for ammonia removal, polysulfide addition for cyanide removal, activated sludge for ammonia or thiocyanate removal, and biological denitrification for nitrate removal. The removal mechanisms vary widely between individual processes. Polysulfide addition, activated sludge, biological denitrification, and ion exchange using a clinoptilolite resin are presented herein as examples of processes for removal of dissolved inorganics.

Polysulfide Addition

Cyanide can be removed from wastewater streams by converting it to thiocyanate. The conversion is prompted by adding a sulfur source as polysulfide, with only uncomplexed cyanide thereby removed. The product, thiocyanate, would likely need to be removed, but unlike cyanide, it is easily biodegraded. Recent bench-scale studies have demonstrated that thiocyanate removals exceeding 95% can be made by a biological system where only the thiocyanate plus ammonia are available as growth substrates.

Petroleum refiners have for some years used polysulfide to convert cyanide to thiocyanate to protect process equipment from cyanide-induced corrosion. No commercial precedent exists for promoting the reaction at the wastewater treatment process level, but EPA-sponsored preliminary lab studies (unpublished) suggested that the cyanide to thiocyanate conversion could be successfully made if the polysulfide is supplied in large excess of its stoichiometric requirement. The reaction rate seems to be sufficiently slow to require large reactor volumes to supply the needed residence time.

The concentration of cyanide in the influent has only limited effect on the process feasibility. With increasing influent concentrations of cyanide, the reaction kinetics become increasingly favorable. It is the concentration of cyanide in the effluent that determines the residence time and therefore the feasibility of the reaction. Preliminary EPA sponsored studies (unpublished) suggest that the process may be impractical for cyanide removals to less than about 10 mg/L.

Polysulfide addition therefore appears usable only for waste streams where the initial cyanide concentration is greater than about 30 mg/L and some benefit can be identified in reducing this concentration to about the 10 mg/l level. Since additional cyanide removal by some other process would probably be required, the feasibility of polysulfide addition would be determined by the economic tradeoffs between it being used in combination with some other process versus the other process being used alone.

Activated Sludge

Certain dissolved inorganics, particularly ammonia and thiocyanate, can be biologically oxidized even in systems where these species are the only growth substrates available for microorganisms. Most of the contaminants are oxidized to supply energies for metabolism while the rest are assimilated as new cell material. Microorganisms may be viewed as catalysts that mediate the oxidation of material that would otherwise oxidize very slowly or not at all.

A variety of physical configurations can be used to provide contact between the microorganisms and the contaminants to be removed, but suspended growth or activated sludge systems are perhaps most common. The cells are dispersed throughout a reactor volume where they contact the incoming waste stream on a continuous basis. Long enough residence time is provided for the microorganisms to degrade the contaminants to an acceptable level. Effluent from the reactor is routed to a clarifier where the suspended cells are separated from the bulk fluid. Concentrated cells are drawn from the underflow of the clarifier, and a fraction are wasted equal to their increase in mass resulting from cell growth in the reactor. The rest, constituting the much larger fraction, are recycled to the reactor. By this process of cell wastage and recycle, a constant.mass of cells can be maintained in the reactor for a controlled period longer than the hydraulic residence time. The period selected is one that is in phase with the optimal life cycle of the cells. The cell residence time is therefore the key process variable as it controls both the overall system performance and stability.

Activated sludge processes designed to oxidize ammonia to nitrate are well established in both industrial and municipal applications. Ammonia destruction at the 98% level are reportedly possible. Recent bench-scale studies have indicated greater than 95% oxidation of thiocyanate and ammonia for biological systems fed a waste stream containing only these two species. This is especially significant since K-T gasification wastewaters consist primarily of cyanides, thiocyanate, ammonia, and more readily oxidizable species such as $S^=$, $SO_3^=$, and $S_2O_3^=$.

As is the case for all processes utilizing the growth reactions of microorganisms, activated sludge processes are subject to upsets when the characteristics of the feed stream vary beyond certain limits. However, activated sludge processes designed to remove ammonia and thiocyanate may be especially prone to upset. In general, most organics that are biodegradable can be oxidized by a wide variety of microbial species in an activated sludge system. Each specie has its particular range of conditions to which it is tolerant, and the individual ranges overlap, forming a much wider spectrum of tolerance than that represented by any one specie. However, ammonia and thiocyanate are oxidized by only a very few, specialized microorganisms. A narrow range of tolerable conditions is represented by these few species, and when conditions fall outside this range, the system fails.

Another problem potentially affecting reliability is associated with operation of the clarifier. Conditions that lead to malfunction of the clarifier are not fully understood. However, where there is relatively constant feed and where the system is otherwise carefully operated, activated sludge should be a reliable process.

Biological Dentrification

In dentrification, nitrate is removed by being reduced to molecular nitrogen which can be vented directly to the atmosphere. Physically the system resembles that of activated sludge, but the removal mechanism is somewhat different. When oxygen is not available, most microorganisms can substitute nitrate as the terminal electron acceptor in their growth and energy reactions. Nitrate is thereby reduced to molecular nitrogen in the denitrification reactor not by being acted on directly but by participating in the oxidation of some other organic substrate. If not otherwise available, a substrate (or carbon source) must be supplied, and methanol is a common choice. Other organic-laden wastes may be used as the carbon source to advantage in a K-T facility.

While less experience exists for denitrification than for activated sludge systems, the process is considered well developed. Nitrate removals of up to 90% are reported in the open literature.

Denitrification is usually a reliable process due largely to the diverse population of microorganisms that are cultured in the reactor. Most reliability problems relate to settleability of biosolids to shock loadings, or to very cold weather.

Ion Exchange

Ion exchange involves a reversible interchange of ions in solution with other ionic species bound to a solid ion exchange medium. Clinoptilolite is a naturally occurring ion exchange material that will selectively exchange its bound sodium or calcium ions for ammonium ions in the contacting solution. Upon initial loading of fresh clinoptilolite, nearly all ammonia is removed from the waste stream. With time, fewer exchange sites are available and increasingly less ammonia can be removed. When the concentration of ammonia escaping the process increases to an unacceptable level, the resin is replaced and regenerated for reuse by contacting it with a strong brine solution. Ammonia rich brine from regeneration is air stripped in a closed loop system. The stripper off-gas is scrubbed by an acid wash to recover the nitrogen as ammonium sulfate before the stripping gas is recycled.

Several complete ammonia removal/recovery systems are in operation for municipal-strength wastewaters. One is a system that has been operated successfully by the Tahoe-Truckee Sanitation Agency. No major problems have reportedly occurred with either the ion exchange units or the regeneration/ammonia recovery units. No known precedent exists for higher strength waste streams. Preliminary lab studies sponsored by EPA suggest that ion exchange would be a feasible process for treating waste streams having ammonia concentrations much higher than that normally associated with municipal wastewaters. It is expected that ammonia can be removed to the 1 mg/l level or less from a waste stream containing ammonia at the 100 to 200 mg/l level.

4.2.1.5 Processes for Removal of Dissolved Organics

A variety of control processes are applicable to wastewater streams requiring removal of dissolved organics. Activated sludge is a commonly used process and is presented as an example in this section.

An activated sludge system designed to remove organics is identical in principal to that discussed for removal of inorganic species (refer to Section 4.2.1.4). Most biodegradable organics can be oxidized by a variety of microbial species. Performance varies widely depending on the characteristics of the wastewater stream, but BOD removals of 80 to 90% or better are typical. Nitrogen and phosphorous in forms usable by the microorganisms are required as growth nutrients, and these elements are assimilated as new cell material.

Microorganisms that utilize organic substrates can sometimes oxidize or otherwise remove a variety of inorganic species concurrently. Even some species such as cyanide that are normally nondegradable can be oxidized. Cyanide removals exceeding 90% have been reported in laboratory-scale tests.

The exact performance of an activated sludge system can be determined with certainty only following bench-scale or pilot testing of the subject wastewater stream. Removal of most inorganic species usually cannot be assessed accurately until after the system is in place.

4.2.1.6 Processes for Removal of Residual Organics

Residual organics occur in wastewater streams due largely to performance limitations of upstream controls. When a biological system is the upstream control, residual organics consist of biodegradable material and a larger fraction of refractory organics that are resistant to biological oxidation. Activated carbon, chemical oxidation, and thermal oxidation are presented herein as examples of processes that can remove residual organics. Most of these systems can also remove residual inorganic species.

Activated Carbon Adsorption

Activated carbon adsorption is a widely used method of removing residual organics from industrial wastewaters. This technology may be applied by one of two methods: 1) the use of powdered activated carbon in conjunction with biological treatment or 2) the direct contact of granular activated carbon with contaminated wastewaters. The direct contact method using granular activated carbon is considered herein.

The activated carbon is contained in a packed bed through which the waste stream is routed under either gravity or pressure flow conditions. Dissolved organics (as well as possibly other dissolved species) are removed from the waste stream by being attached to adsorption sites on the carbon. The adsorptive capacity of the bed is a function of the organic loading, the contact time in the bed, and the affinity of the carbon for the organics.

The carbon bed requires regeneration when its adsorptive capacity is reached. Systems requiring more than 225 to 450 kg of carbon per day can be economically regenerated on-site. Regeneration is a thermal process that requires approximately 10 MJ per kilogram of carbon regenerated. Approximately 2 to 10 percent of the activated carbon is lost due to physical attrition and oxidation. Both the thermal regeneration energy and makeup carbon required to replenish regeneration losses are predominant factors in the overall economics of carbon treatment processes.

Removal of any contaminant species is highly stream- and carbon-specific. A particular species may be sorbed by the carbon differently with varying concentrations and characteristics of other species present in the waste stream. Designs for activated carbon systems must therefore rely heavily on direct testing of the actual wastewater stream.

Chemical Oxidation

Many chemical species are less reactive or otherwise less objectionable to the environment when they are oxidized to their highest state. The process of chemical oxidation consists of driving these reactions by adding a suitable oxidizing agent.

Chemical oxidation is typically carried out in specially designed, closed contactors when the oxidant is a gas and in stirred reactors when the oxidant is a liquid. A variety of chemical oxidants can be used, but ozone, chlorine, chlorine dioxide, and hydrogen peroxide have widest application.

Both organic and inorganic species are oxidized during chemical oxidation. The extent of removal is highly dependent on the oxidant used, concentration of the contaminant, complexity of the molecule to be oxidized, reaction time, extent of reactor mixing, pH, and temperature.

Chemical oxidation is most commonly used to remove low level concentrations of chemical species. For the stronger oxidants such as ozone and chlorine, generally all materials in the waste stream are attacked, and each species is removed approximately in order of its amenability to oxidation. Thus if chemical oxidation is used with the intention to remove a particular species, say cyanide, the presence of other oxidizable material in the waste stream may greatly increase the demand for the oxidant above that which would otherwise be required.

The equipment used for chemical oxidation with Cl_2 and lime is typically simple and therefore expected to be highly reliable. While no known experience exists for treating wastewaters from coal gasification facilities, the process has been used extensively in other applications. Chemical oxidation and the closely related process of disinfection have shown reliable performance treating municipal strength wastewaters over many years of service. Similar performance is expected in coal gasification applications.

Thermal Oxidation

Thermal oxidation or incineration is a high temperature process for the destruction of a variety of wastewater contaminants. Wastewater incineration can be considered a combination of evaporation, pyrolysis, and oxidation although oxidation is the primary process leading to the ultimate destruction of most toxic pollutants. Pyrolysis, or destructive distillation, is a process in which heat breaks down the waste material into simpler components which can either be recovered or oxidized more easily than the original material. Oxidation, or combustion, promotes the reaction of waste components or pyrolysis products with oxygen to form such products as carbon dioxide, water, and oxidized inorganics such as sulfates and nitrates.

Thermal oxidation is capable of treating a variety of organic-laden wastes. Wastes having a high energy content are self-sustaining, that is, their oxidation liberates sufficient energy to raise the waste temperature to the temperatures required to sustain the oxidation reactions and drive them to completion. Low energy wastes require addition of auxiliary fuel. Preconcentration of a low energy aqueous waste may also be used to reduce or eliminate the need for an auxiliary fuel.

Thermal oxidation is capable of achieving essentially complete destruction of a wide range of otherwise difficult to treat organics. Most organics can be completely destroyed at 1300K with two seconds residence time. Tests with various pesticides such as DDT, malathion, and chlordane have shown 99.96 to 99.99 percent destruction. Tests at commercial hazardous waste incinerators have shown over 99.99 percent destruction of PCBs. Many incinerators have been operated reliably for years without shutdowns.

4.2.1.7 Processes for Volume Reduction

Most volume reduction processes are capital and energy intensive, but their application can sometimes be justified by the economics of ultimate disposal. An exception is cooling tower concentration which has little or no associated capital charge since the cooling tower is an integral part of the base plant. Cooling tower concentration and forced evaporation are presented as examples of volume reduction processes.

Cooling Tower Concentration

Based upon the availability of cooling water at the plant site and the overall wastewater treatment strategy, process wastewater may be used as partial makeup to the cooling towers. This practice results in a reduction in wastewater volume due to evaporative concentration. Concentration increases of 4 to 5 times that of inlet water are common for the blowdown from conventional cooling towers, representing a 75 to 80% volume reduction. If organics are present in the feed, some will be oxidized in the tower by both biological activity and direct combination with oxygen.

In some applications, cooling tower concentration may not be feasible. Potential problems include excessive biological growth and fouling, corrosion, scaling, and loss of volatile species. Each of these can be corrected by appropriate pretreatment, but at some point the additional cost of pretreatment steps exceed the value of benefits derived from cooling tower concentration.

Forced Evaporation

Forced evaporation of a wastewater stream can be accomplished by one of two principal systems. Of these, vapor compression evaporation has lower energy costs and will be discussed for purposes of this manual.

In the vapor compression evaporation process, vaporization energy is supplied by a mechanical compressor. The compressor raises the temperature and pressure of the vapor from a tubeside evaporator, and steam is condensed on the shellside of the evaporator, boiling more water. Seed crystals are maintained in the evaporator to prevent scaling by the supersaturated liquor.

The evaporation overhead may be of sufficient quality to recycle directly to the plant. The blowdown is typically 2 to 10% of the total wastewater flow and contains the original contaminant species concentrated into this small flow.

Vapor compression evaporators are sensitive to dissolved gases and volatile organic compounds in the feed. Volatile components will appear in the overhead and may require control. Such components may also affect recovered water quality and limit its direct reuse within the facility.

4.2.1.8 Methods of Residual Disposal

Most commonly, treated wastewaters are discharged to a receiving body for ultimate disposal. Constraints of such discharges are highly site-specific and beyond the scope of this manual. There are several other methods that can be used to dispose of a waste stream after it has been handled by appropriate upstream controls. Deep well injection, surface impoundment, and co-disposal with ash are presented as examples.

Deep Well Injection

Deep well injection has been used to dispose wastes that are difficult to treat such as those containing high total dissolved solids or those containing organics like tert-butyl alcohols (nonbiodegradable) and ketones (not amenable to activated carbon adsorption). The disposal system consists of a surface facility for pretreatment, a well, and a disposal zone. Many types of formations can, under favorable circumstances, have sufficient porosity and permeability to accept large quantities of injected liquid wastes. In practice, most wells have been constructed to inject into sand or sandstone and limestone or dolomite. Detailed geological and engineering studies are required to determine the suitability of a potential site.

The injection depth is generally selected to provide adequate separation from potable subsurface water. In every case, injection zones for disposing of hazardous wastes must be below the deepest underground source of drinking water. Wells are usually cased and cemented to prevent the upward migration of fluids that are injected through tubing in a packer set immediately above the injection zone. Injection pressures are set to ensure that neither fracture nor fluid migration occur.

The major advantages of deepwell injection are: 1) it is an ultimate disposal method, 2) it requires little land, and 3) it removes the waste from contact with air, surface water, usable ground water, and the surface of the ground. Major disadvantages include: 1) long-term effects are largely unknown and difficult to predict, 2) control over the waste may possibly be lost after injection, 3) favorable geologic conditions may not be available in the vicinity of the waste source, 4) pretreatment adds to the expense of waste disposal, and 5) wastes with high organic loading may cause plugging of the well formation.

Deepwell injection has seen limited use in the disposal of industrial wastes for over 25 years. However, a large number of wells inject oil field brines. Performance data for a number of the industrial wells has shown failures as well as successes. Problems have included migration of waste to usable aquifers as a consequence of fracturing, faults in confining strata, or defects in well casings.

Surface Impoundment

Surface impoundments are widely used to treat/dispose of industrial wastes. These impoundments (also known as holding basins, lagoons, oxidation ponds, settling basins, and evaporation ponds) can be either natural or man-made reservoirs to which wastewaters, slurries, or sludges are discharged. Retention time in the impoundment provides for natural evaporation, settling of solids, biological decomposition of organics, and possible loss of volatile components of the wastes. If properly designed and operated, minimal environmental contamination should occur.

The suitability of a surface impoundment depends on site-specific factors. For example, in order to successfully serve as an evaporation pond, a surface impoundment must be located at a site having a sufficiently high net evaporation rate. A major drawback to their use is the need for relatively large areas of land.

Co-disposal of Wastewater Streams with Ash

Co-disposal is an ultimate disposal method wherby the wastewater stream is sorbed by ash, then the ash is handled by an appropriate solid waste disposal method. The feasibility is determined by the quantity of ash generated, its sorptive capacity, and the volume reduction needed to match the flow of the wastewater stream to that which can be sorbed by the ash. All constituents in the wastewater stream become entrained in the ash, except those that might volatilize in the course of wastewater/ash mixing.

4.2.2 Water Pollution Controls for Streams Containing Predominantly Organic Constituents

Wastewater streams that contain predominantly organic constituents are the condensates from the synthesis operation: Mobil M synthesis condensate (Stream 233), F-T synthesis condensate (Stream 223), or methanol distillation condensate (Stream 229). Control processes applicable to these streams are discussed in this section. In all likelihood, none of these streams would be treated individually, but as a consequence of economics, each would be combined with others for common treatment. Therefore, the following discussion of individual stream controls is necessarily in the context of composite streams.

None of the water pollution control technologies discussed in this section would be singularly applied to a particular composite waste stream. Various combinations of controls would be used, and the wastewater characteristics input to an individual control would not necessarily be those of the raw composite flow but those modified by other, upstream processes. The emphasis in this section, however, is on individual controls, and as such, inputs (and therefore performances) are estimated as those being most likely to occur.

Neither the flow nor the loading of wastewater streams from the synthesis sections are specific to the type of coal fed to the gasifier. However, waste stream quality and quantity originating from the gasification section are specific to both coal type and process design, and these streams contribute to the composite flow of which synthesis condensate is a part. In this sense, coal type and gasification train design affect the choice and cost of water pollution controls. A more detailed discussion of the effect of coal type on wastewater streams is provided in Section 4.2.3.

4.2.2.1 Mobil-M Synthesis Condensate (Stream 233)

The waste stream from the Mobil M synthesis section (Stream 233) would probably be combined with the compression condensate (Stream 211) and the gas cooling/dust removal blowdown (Stream 210) from the gasifier section for common treatment. As discussed in Section 3.3.4, base plant designs may utilize either a methanol- or water-based wash to remove cyanide from the raw gas. In cases where a water-based wash is used, an additional wastewater stream would be generated which could also be combined with the three waste streams.

This section considers individual water pollution control technologies that are applicable to the Mobil M synthesis condensate where it is part of a composite flow described for base plants utilizing either a methanol- or water-based cyanide wash. Each technology has been discussed in Section 4.2.1. Only details specific to the subject composite flow are presented herein.

Activated Sludge

Activated sludge could be used to remove dissolved organics and other contaminant species from the composite waste stream. For facilities utilizing a water-based cyanide wash, organics expressed as BOD are estimated to be 1100 mg/L in a flow of about 688 m^3/hr. Activated sludge by one or more stages is expected to remove BOD to about the 35 mg/L level with all reduced sulfur species removed to 1 mg/L.

For facilities utilizing a methanol-based cyanide wash, the Mobil M condensate would be part of a smaller composite flow, about 449 m^3/hr. Without the dilution of the cyanide wash water, the BOD concentration in the composite flow would be higher at about 1700 mg/L (but same loading) and removed to about the 40 mg/L level. All other species would be removed to approximately the same extent as those cited for the water-based, cyanide wash case.

Much of the ammonia needed to supply nitrogen as a growth nutrient would be present in the waste stream. However, supplemental ammonia as well as phosphorus and possibly trace amounts of other materials would be required.

Due to the usual variability of waste stream characteristics, precise addition of ammonia would not be practical, and some overdosing would be required. All ammonia added in excess of that required for cell growth would appear in the activated sludge effluent.

Cyanide is normally considered toxic to microorganisms, but when it occurs as part of a larger matrix of biodegradable organics, the resulting microbial population can often acclimate to the stress of cyanide and oxidize or otherwise remove some of it. Greater than 90% removal has been recorded in carefully controlled, laboratory-scale studies. The exact removal that would be realized is highly uncertain and can be determined only once the system is in place.

A secondary waste stream would be generated consisting of biological solids drawn from the underflow of the clarifier (Stream 415). This stream would have a solids content of about 1 to 2% with a dry solids flow of about 12,700 kg/d for base plant designs using a water-based cyanide wash. For the methanol-based case, the dry solids flow would be about 12,300 kg/d. Following concentration to about 20 to 40% dry solids, the solid waste stream would be handled by one of the methods discussed in Section 4.3.

A secondary waste stream consisting of volatile species escaping the activated sludge reactor (fugitives) may also be generated (Stream 416). This stream is considered further in Section 4.2.4.

Total capital investment for activated sludge is estimated to be $18.3 million with a total annualized cost of $3.9 million.

Filtration

Filtration could be used to remove suspended solids from the composite wastewater stream. For base plant designs utilizing a water-based cyanide wash, the flow of the composite stream is expected to be about 688 m^3/hr, while a flow of about 449 m^3/hr is expected for the methanol-based case. For both cases, the filter would be utilized following upstream treatment processes, and an influent suspended solids concentration of about 30 mg/L is expected with most of this material consisting of biological solids. Filtration should remove the suspended solids to less than 10 mg/L.

A secondary waste stream of filter backwash (Stream 417) would be generated on an intermittent basis. This stream would range between 2 and 10% of the influent flow and would contain most of the material that was removed during the preceding filter run. The filter backwash is a small volume stream, but its high loading prevents it from being routed directly to other control processes for treatment. The backwash would therefore be routed to either its own or some other flow equalization facility for gradual release to other water control processes.

Total capital investment and total annualized cost for filtration are estimated to be \$1.2 and \$2.6 million for the water-based cyanide wash case and \$0.78 and \$1.8 million for the methanol-based cyanide wash case.

Granular Activated Carbon

Granular activated carbon could be used to remove residual organics following upstream treatment processes. For the water-based cyanide wash case, the flow of the composite wastewater stream would be about 688 m^3/hr with a COD of about 680 mg/L. COD removals to approximately 70 mg/L are expected. For base plant designs utilizing a methanol-based cyanide wash, the flow of the composite stream would be about 449 m^3/hr, and a COD of about 1060 mg/L would be reduced to approximately 100 mg/L.

Regeneration of activated carbon by standard thermal methods would generate an offgas (Stream 420). Control of this stream would probably be a function integral with the regeneration facility design.

Total capital investment and total annualized cost for the granular activated carbon process are estimated to be \$3.1 and \$1.5 million for the water-based cyanide wash case and \$3.0 and \$1.6 million for the methanol-based cyanide wash case.

Cooling Tower Concentration

Cooling tower concentration could be utilized to reduce the volume of the composite wastewater stream to be handled for disposal. The feasibility of this control would have to be evaluated on an individual case basis. Certain species in the subject waste stream including biodegradable organics, chloride, TDS, calcium, and sulfate may cause excessive fouling by biological growth, corrosion, or scaling.

Loss of volatile species stripped from the wastewater stream is a secondary waste stream (Stream 419) and another factor that may limit the feasibility of cooling tower concentration. In particular, ammonia and hydrogen cyanide may be lost to the atmosphere, but the exact amount as well as the amount that would be permissible in a given location is uncertain.

For base plant designs using a water-based cyanide wash, the composite wastewater stream could supply 688 m^3/hr of the 920 m^3/hr makeup flow to the cooling tower. All species in the original wastewater stream would be concentrated by a factor of 3.8 into the 180 m^3/hr blowdown, assuming minimal losses by volatilization or drift. The corresponding makeup contribution and concentration factor for the methanol-based case would be 449 m^3/hr and 2.5 respectively.

Characteristics of the composite wastewater stream used as partial makeup to the cooling tower are those that have been modified by upstream treatment processes. These feed and the resulting blowdown characteristics are summarized in Table 4-27. Since the cooling tower is considered part of the base plant, no capital costs associated with environmental controls are assumed to be required.

TABLE 4-27. MATERIAL FLOW FOR COOLING TOWER CONCENTRATION - MOBIL M SYNTHESIS CASE

Base Plant Cyanide Wash:	Water-based		Methanol-based	
Characteristic*	Makeup†	Blowdown†	Makeup†	Blowdown†
Flow (m^3/hr)	688	180	449	180
NH_3	10	38	10	25
CN^-	9-35	34-130	1	2
$S^=$	<1	<1	<1	<1
$S_2O_3^=$	<1	4	<1	2
$SO_3^=$	<1	4	<1	2
SCN^-	<1	4	<1	2
COD	680	2600	1060	2650
BOD_5	35	130	42	105
Cl^-	1040	3900	1600	4000
TDS	1900	7200	2900	7200
TSS	30	110	30	75

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

†This stream combined with another source to supply the total makeup requirement of 920 m^3/hr.

Forced Evaporation

Forced evaporation could be used to decrease the volume of the composite wastewater flow by concentrating the contaminant species into a fraction of the original volume. Condensate from forced evaporation may contain compounds volatilized during water evaporation. Volatilized components may influence condensate reuse alternatives, depending upon which compounds are volatilized and their concentrations in the condensate. For material balance purposes, volatilization was neglected since no data are available to support assumptions relating to species losses from the feed. The feasibility of this control process would have to be evaluated on an individual case basis.

Forced evaporation would be preceeded by other control processes for dissolved gas or volatile organics removal. Estimated characteristics of the composite wastewater stream input to forced evaporation and its blowdown are presented in Table 4-28. The estimated blowdown quality represents the worst case for the specified feed and volume reduction since species volatilization has been neglected. Total capital investment is estimated to be $13.7 million with a total annualized cost of $3.5 million.

Incineration

Incineration could be used to remove residual organics following various pretreatment and concentration steps. For the subject composite wastewater stream, the flow to be incinerated would be first decreased by upstream controls to about 18 m^3/hr for both the methanol- and water-based cyanide wash cases. Incineration would reduce COD and BOD in the composite flow from approximately 26,000 and 1000 mg/L to 25 and 1 mg/L, respectively.

Incineration would generate both a liquid and a gaseous secondary waste stream. The gaseous stream is flue gas (Stream 421) from combustion of auxiliary fuel and waste stream constituents. This stream would be controlled by equipment that is an integral part of the incinerator facility. The liquid stream is the flue gas quenching/scrubbing system blowdown. This stream would have a low flow and contain mainly inorganic salts with some particulate material. It would be routed to other processes for treatment or combined directly with the effluent stream.

Total capital investment for incineration is estimated to be $4.8 million with a total annualized cost of $2.3 million.

TABLE 4-28. MATERIAL FLOW FOR FORCED EVAPORATION-
MOBIL M SYNTHESIS CASE

Base Plant Cyanide Wash:	Water-based		Methanol-based	
Characteristic*	Input	Blowdown†	Input	Blowdown†
Flow (m^3/hr)	180	8	180	18
NH_3	38	380	25	250
CN^-	34-130	340-1300	2	20
$S^=$	<1	<1	<1	<1
$S_2O_3^=$	4	40	2	20
$SO_3^=$	4	40	2	20
SCN^-	4	40	2	20
COD	2600	26000	2650	26500
BOD_5	130	1300	105	1050
Cl^-	3900	39000	4000	40000
TDS	7200	72000	7200	72000
TSS	110	1100	75	750

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

†Blowdown quality represents the worst case for the specified feed and volume reduction since species volatilization has been neglected.

4.2.2.2 F-T Synthesis Condensate (Stream 223)

The characteristics of the F-T synthesis condensate (Stream 223) are somewhat different than those of the Mobil M condensate (refer to Section 3.4.6), but a similar treatment approach would be involved. Applicable control processes are discussed in Section 4.2.2.1 with costs and performances varying only slightly from those presented as a primary result of flow rate differences. For example, an activated sludge system designed to treat the F-T synthesis condensate is estimated to require a total capital investment of $20.9 million, an increase of about 14% over the equivalent Mobil M activated sludge system.

4.2.2.3 Methanol Distillation Condensate (Stream 229)

The methanol distillation condensate (Stream 229) combined with gasification wastewaters contains sufficient loading of organics to be handled analogously to the Mobil M or F-T synthesis cases. However, the nitrogen (as ammonia) in the inorganic streams would greatly exceed the amount needed for biological oxidation of the organics. The methanol condensate could also be handled by slight modification to control technologies discussed in Section 4.2.3.1 for base plant cases where cyanide is removed from the raw gas by a water wash, and in Section 4.2.3.2 for the methanol wash case.

4.2.3 Water Pollution Controls for Streams Containing Predominantly Inorganic Constituents

Wastewater streams that contain predominantly inorganic constituents are the cyanide wash water (Stream 215), primary compression and cooling condensate (Stream 211), and the gas cooling and dust removal blowdown (Stream 210). It is not likely that any of these streams would be treated separately, but each would be combined with the others, for reasons of economics, into a composite flow. Paralleling the approach taken in Section 4.2.2, each stream is discussed in this section in the context of a composite flow.

4.2.3.1 Cyanide Wash Water (Stream 215)

A number of control processes are applicable to the cyanide wash water (Stream 215). Of these, only polysulfide addition would be applied exclusively to this stream. All other processes would be applied to a composite wastewater stream consisting of the combined flows of the cyanide wash water (Stream 215), the compression condensate (Stream 211), and the gas cooling/dust removal blowdown (Stream 210). Each of the control technologies considered in this section has been discussed in Section 4.2.1, and only details specific to the subject composite flow are considered in the following subsections.

Polysulfide Addition

Polysulfide could be added to the cyanide wash water to convert cyanide to thiocyanate. The cyanide wash is estimated to have a flow of 239 m^3/hr with a cyanide concentration of 240 mg/L. Less than about 10 mg/L cyanide is expected to remain following polysulfide addition to a flash mix reactor and subsequent reaction in a plug flow reactor. This performance is estimated assuming that little of the cyanide is present in a complexed form, an expectation based on estimated very small concentrations of potentially complex-forming cations in the subject waste stream.

Preliminary EPA sponsored lab studies (unpublished) indicate that the conversion of cyanide to thiocyanate can be accomplished at the wastewater treatment process scale. However, excess polysulfide of approximately double its stoichiometric requirement may be needed to achieve reasonably rapid reaction rates. Otherwise, residence times and therefore reactor volumes may assume unreasonable dimensions.

In some applications, it may be possible to dose polysulfide directly to the cyanide wash circuit (or alternatively to the gas cooling/dust removal circuit). If feasible, substantial cost savings would be realized. Most capital requirements would be eliminated as a small modification to the cyanide wash system would replace the large treatment wastewater reactors. More importantly, it is expected that the polysulfide demand would be reduced. Nearly complete conversions of cyanide are realized in refinery applications where approximately stoichiometric doses of polysulfide are made at the outlet of process equipment. It is therefore expected that by dosing the polysulfide directly to the cyanide wash circuit or to the gas cooling/dust removal circuit, nearly complete cyanide conversions could likewise be realized with a minimum of polysulfide added.

Another method of effecting cyanide conversion by polysulfide might be to add the polysulfide in conjunction with another wastewater treatment process. A likely prospect is the activated sludge process, but this configuration has never been tried.

The cyanide to thiocyanate conversion has generally been identified as requiring alkaline reaction conditions. Following polysulfide addition, the subject waste stream would be combined directly with the compression condensate and the gas cooling/dust removal blowdown, or if sufficent acidity is not available in these streams, the cyanide wash would be first neutralized with acid. In either case, the pH of the cyanide wash will be depressed to approximately neutral and unreacted polysulfide may precipitate. In some cases, this precipitate may be compatible with downstream controls. If not, a filter or clarifier would be added.

Total capital investment for polysulfide addition is estimated to be $130,000 with a total annualized cost of about $730,000.

The type of coal fed to the gasifier is expected to have little effect on the mass flow of cyanide produced in the gasifier section. The flow and cyanide concentration of the cyanide wash will therefore by generally independent of coal type, and the cost of polysulfide addition will remain constant as well.

Activated Sludge

Activated sludge would be utilized primarily to oxidize ammonia and thiocyanate, although other species would be removed as well. The subject composite wastewater stream would contain about 260 mg/L of ammonia and 210 mg/L of thiocyanate, at 578 m^3/hr. Following activated sludge, about 8 mg/L ammonia and less than 1 mg/L thiocyanate are expected to remain.

A secondary waste stream of biological solids (Stream 415) at about 1% concentration would be drawn from the underflow of the clarifier at the rate of about 1300 kg/d dry solids. Following concentration to 20 to 40% solids by a filter press or other solids handling equipment, this waste stream would be handled by appropriate solid waste disposal techniques discussed in Section 4.3.

Total capital investment is estimated to be $12.6 million with a total annualized cost of about $2.7 million.

Denitrification

Denitrification could be utilized to remove nitrate. The process would be preceeded by other controls such that the composite wastewater stream would contain a nitrate concentration of about 245 mg/L at 578 m^3/hr. Denitrification is expected to remove nitrate to about the 25 mg/L level.

A secondary waste stream of biological solids (Stream 418) at about 1% concentration would be drawn from the underflow of the clarifier at the rate of about 1800 kg/d dry solids.

Total capital investment is estimated to be $6.1 million with a total annualized cost of about $2.2 million.

Filtration

Details of filtration are identical to those presented in Section 4.2.2.1. The composite wastewater stream has a flow of about 578 m^3/hr. The total capital investment was estimated to be $1.0 million with a total annualized cost of about $220,000.

Chemical Oxidation

Chemical oxidation could be used to remove low level concentrations of cyanide that remain in the composite wastewater stream following treatment by other controls. However, since cyanide is a slowly oxidized species, most other reduced chemical species would be removed concurrently, increasing the oxidant demand. The composite wastewater stream with a flow rate of 578 m^3/hr would probably contain less than 10 mg/L of both cyanide and ammonia. Both would be removed to less than 1 mg/L.

Total capital investment is estimated to be $720,000 with a total annualized cost of $230,000.

Ion Exchange for Ammonia Removal

Ion exchange using a clinoptilolite resin could be utilized to remove ammonia. When applied to the 578 m^3/hr composite wastewater stream containing 260 mg/L ammonia, ion exchange is estimated to be capable of reducing the ammonia concentration to less than 10 mg/L.

Total capital investment is estimated to be $12.9 million with a total annualized cost of about $3.5 million.

Cooling Tower Concentration

Cooling tower concentration could be utilized to reduce the volume of the composite wastewater stream to be handled by downstream processes and disposal methods. Since the subject waste stream is essentially free of organics, fouling by biological growth is not expected to be a problem. However, other characteristics of the waste stream may be limiting, and the applicability of cooling tower concentration would therefore have to be determined on an individual case basis.

The makeup required for the cooling tower (methanol synthesis case) is 825 m^3/hr. The composite waste stream at 578 m^3/hr could supply most of this with the balance supplied by other sources. With blowdown at 161 m^3/hr, chemical species in the original wastewater stream would be concentrated by a factor of 3.6, assuming minimal loss of species by volatilization and drift. The characteristics of the composite waste stream when used as cooling tower makeup, and therefore of the blowdown, will vary depending on the upstream control processes applied. The makeup and blowdown characteristics summarized in Table 4-29 are estimated as worst case examples. Since the cooling tower is part of the base plant, no costs associated with environmental controls have been estimated for it.

Forced Evaporation

Forced evaporation could be used to decrease the volume of the composite wastewater stream. Forced evaporation would also permit recovery of a high quality steam suitable for recycle to the base plant. The feasibility of this control process would have to be evaluated on an individual case basis.

As with cooling tower concentration, the characteristics of the input to forced evaporation and its blowdown would vary with upstream controls. Estimated worst case characteristics are presented in Table 4-29.

Total capital investment is estimated to be $13.7 million with a total annualized cost of about $3.5 million.

TABLE 4-29. MATERIALS FLOW FOR COOLING TOWER CONCENTRATION AND FORCED EVAPORATION - WATER-BASED CYANIDE WASH CASE

	Cooling Tower Concentration		Forced Evaporation	
Characteristic*	Make-up†	Blowdown	Feed	Blowdown
Flow (m^3/hr)	578	161	161	16
NH_3	260	933	933	9330
CN^-	7.5	27	27	270
$S^=$	2	<1‡	<1	<1
$S_2O_3^=$	58	205	205	2050
$SO_3^=$	14	50	50	500
SCN^-	210	740	740	7400
Cl^-	1200	4500	4500	45000
TDS	2200	7900	7900	79000
NO_3^--N	245	880	880	8800
TSS	30	110	110	1100

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

†This stream combined with another source to supply the total makeup requirement of 825 m^3/hr.

‡$S^=$ is lost through both oxidation and stripping.

4.2.3.2 Raw Gas Compression and Cooling Condensate (Stream 211)

The compression condensate (Stream 211) could be combined with the cyanide wash water (Stream 215) and the gas cooling/dust removal blowdown (Stream 210) for common treatment. In this context, control technologies applicable to the compression condensate are identical to those presented for the cyanide wash water, Section 4.2.3.1 with exception of polysulfide addition. The characteristics of all waste streams and the performances and costs of all controls are the same.

As discussed in Section 3.3.4, some base plant designs may use a methanol- rather than water-based wash to remove cyanide from the raw gas. Where this option is exercised, the compression condensate would probably be combined only with the gas cooling/dust removal blowdown for common treatment since no cyanide wash water would be generated. The control technologies discussed in Section 4.2.3.1 would still be applicable to this composite flow, but with different waste stream characteristics, certain performances and costs would be different. This section considers only aspects of the control technologies applied to the subject composite stream (i.e., compression condensate and gas cooling/dust removal blowdown) that differ from those already presented in Section 4.2.3.1.

Activated Sludge

The composite wastewater stream is estimated to contain about 190 and 4.5 mg/L of ammonia and thiocyanate, respectively, and has a flow rate of 339 m^3/hr. Ammonia would be removed to about 6 mg/L and thiocyanate removed to less than 1 mg/L. A biological solids waste stream (Stream 415) would be generated at a rate of 270 kg/d dry solids in a 1 to 2% solids slurry. This solid waste stream would be concentrated to 20 to 40% solids by a filter press or some other control, then disposed of by a method described in Section 4.3.

Total capital investment is estimated to be \$6.7 million with a total annualized cost of about \$1.5 million.

The composition of the compression condensate and therefore the characteristics and costs of applicable controls are affected by the type of coal fed to the gasifier. As discussed in Section 3.2.1, ammonia formation during gasification tends to increase with decreasing coal rank. Therefore the quantity of ammonia in the compression condensate and/or the gas cooling/dust removal blowdown, which also contributes to the composite flow, would likewise increase for lower rank coals, and there would be a corresponding increase in the total capital investment and total annualized cost of water pollution controls.

Coal chloride content has little effect on the characteristics of the compression condensate since halogens are almost completely removed during gas cooling and dust removal. However the characteristics of the gas cooling/dust removal blowdown and therefore the characteristics of the subject composite stream are dependent on coal type. These aspects are considered in Section 4.2.3.3.

Biological Denitrification

Denitrification would be applied to the composite waste stream following upstream treatment processes. From a flow of 339 m^3/hr, the concentration of nitrate could be decreased from about 140 mg/L to 15 mg/L. Total capital investment is estimated to be \$3.2 million with a total annualized cost of \$980,000.

A biological solids waste stream (Stream 418) would be generated at a rate of about 590 kg/d dry solids in a 1 to 2% solids slurry. Following dewatering to 20 to 40% solids, the waste stream would be disposed of by a solid waste disposal method described in Section 4.3.

Filtration

Total capital investment for filtration of the composite stream of 339 m^3/hr is estimated to be $590,000 with a total annualized cost of about $150,000. All other aspects of filtration are identical to those presented in Section 4.2.2.1.

Chemical Oxidation

When applied to the composite wastewater stream following upstream treatment processes, the chemical oxidation feed would contain approximately 6 and 7 mg/L of ammonia and cyanide, respectively, and has a flow rate of 339 m^3/hr. Each of these species would be reduced to less than 1 mg/L. Total capital investment is estimated to be $160,000 with a total annualized cost of about $350,000.

Ion Exchange

When applied to the composite wastewater stream, the clinoptilolite-based ion exchange system would be loaded with about 190 mg/L of ammonia at 339 m^3/hr. The effluent from this process is expected to contain less than 10 mg/L ammonia. Total capital investment is estimated to be $8.3 million with a total annualized cost of about $1.8 million.

Cooling Tower Concentration

The composite wastewater stream could supply 339 m^3/hr of the 825 m^3/hr required for cooling tower makeup. With blowdown at 161 m^3/hr, constituents in the composite stream would be concentrated by a factor of 2.1. As described in Section 4.2.3.1, the characteristics of the subject composite flow used for makeup water and therefore characteristics of the blowdown would vary according to upstream controls. The makeup and blowdown characteristics summarized in Table 4-30 are estimated worst case examples. No capital cost associated with environmental controls is assumed for cooling tower concentration since the cooling tower is part of the base plant.

Forced Evaporation

As with cooling tower concentration, the characteristics of the input to forced evaporation and its blowdown would depend on upstream controls. Estimated worst case characteristics are presented in Table 4-30. Total capital investment is estimated to be \$13.7 million with a total annualized cost of about \$3.5 million.

TABLE 4-30. MATERIAL FLOW FOR COOLING TOWER CONCENTRATION AND FORCED EVAPORATION - METHANOL-BASED CYANIDE WASH CASE

	Cooling Tower Concentration		Forced Evaporation	
Characteristic*	Make-up[†]	Blowdown	Feed	Blowdown
Flow (m^3/hr)	339	161	161	16
NH_3	190	400	400	4000
CN^-	7	15	15	150
$S^=$	3.5	<1[‡]	<1	<1
$S_2O_3^=$	98	205	205	2050
$SO_3^=$	24	50	50	500
SCN	4.5	9.5	9.5	95
Cl^-	2100	4400	4400	44000
TDS	3800	8000	8000	80000
NO_3^--N	140	300	300	3000
TSS	30	60	60	600

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

[†] This stream combined with another source to supply the total makeup requirement of 825 m^3/hr.

[‡] $S^=$ is lost by both oxidation and volatilization.

4.2.3.3 Gas Cooling and Dust Removal Blowdown (Stream 210)

The gas cooling and dust removal blowdown (Stream 210) could be combined with the compression condensate (Stream 211) for common treatment. Applicable control technologies and corresponding characteristics are discussed in Section 4.2.3.2. For base plant designs where cyanide is removed from the raw gas by a water-based wash, the cyanide wash water (Stream 215) would also be combined with the two streams cited. Applicable control technologies and corresponding characteristics are discussed in Section 4.2.3.1.

The characteristics of the coal fed to the gasifier affect the characteristics of the gas cooling/dust removal blowdown in one of two general ways. First, the mass of ammonia produced in the gasifier tends to increase with decreasing coal rank. Also, higher sulfur levels generally result from coals having higher sulfur contents, although certain secondary effects such as ash alkalinity may have more of an affect on the sulfur contained in wastewater streams. The level of cyanide in wastewater streams is affected only slightly by characteristics of the coal.

Second, coal type can affect the quantity of water blown down from the gas cooling/dust removal circuit. A minimum blowdown is required representing the difference between the water entering the circuit with the raw gas and that leaving the system with the cooled gas and dust (after dewatering). Most of the water contained in the raw gas is the result of the gas being quenched at the gasifier outlet to reduce its temperature to below the ash fusion temperature so that fouling of the waste heat boiler does not occur. The amount of water added depends on the gasification temperature (a function of coal rank and ash properties) and to a lesser extent on the mass of ash to be quenched.

Blowdown requirements are also influenced by the chloride content of the coal. Chloride in the coal is almost entirely gasified and is recovered in the gas cooling and dust removal operation. If the concentration of chloride in the gas cooling/dust removal circuit exceeds the level considered allowable for operating reasons, makeup water must be added to dilute the chloride concentration, and an increase in blowdown results.

The following two examples demonstrate the effect of coal chloride. For the base case utilizing the Illinois No. 6 coal described in Section 3 and for no makeup water added to the gas cooling/dust removal circuit, the chloride would establish itself in the circuit at about 6000 mg/L. For purposes of this manual, it was assumed that operating requirements of the gas cooling/dust removal circuit impose a chloride concentration limitation of about 2100 mg/L. Makeup water was, therefore, added to dilute the chloride resulting in an increase in blowdown by a factor of about 2.8. If an actual design assumes a significantly different concentration of chloride in the gas cooling/dust removal circuit, the blowdown will change accordingly. The concentration of all species for any composite wastewater stream of which the blowdown is a part would be affected, but the mass loading of all species would remain essentially unchanged. Some modification of individual pollution controls might be needed, but the overall approach to wastewater control and the costs would not be greatly affected.

The blowdown flow rate may also be dependent upon the chloride content of the feed coal. For a system gasifying essentially the same Illinois No. 6 coal but which has one quarter the chloride content (0.07% dry basis) indicated for the design coal, no makeup would be required to the circuit (assuming a maximum permissible chloride level of 2100 mg/L), and the blowdown would decrease by a factor of 2.8.

4.2.3.4 Secondary Waste Streams from Other Media

Secondary waste streams from other media are limited to condensates and purge streams from tail gas treatment processes and purge streams from flue gas desulfirization processes. Estimated flows from these controls are: 4 m^3/hr from Beavon (Stream 405) and SCOT (Stream 409); 3 m^3/hr from Wellman-Lord (Stream 411); and 37.5 m^3/hr from flue gas desulfurization (Stream 425) in the F-T synthesis case and 6.1 m^3/hr in the Mobil M case. Additionally, a waste stream of about 2 to 3 m^3/hr would be generated by the Beavon process consisting of Stretford solution purge (Stream 405). Each of these wastewater streams would either be combined with other streams for common treatment or be treated separately by controls that are well developed in petroleum refining applications.

4.2.4 Integrated Pollution Control Examples

Previous sections have considered individual water pollution controls applicable to the principal wastewater streams generated by a K-T gasification facility. Section 4.2.2 considered streams having predominantly organic constituents and Section 4.2.3 considered streams having predominantly inorganic constituents. Details of individual controls or combinations of controls have not yet been proposed for K-T-based gasification facilities in the U.S. Except where otherwise noted, individual controls have been selected on the basis of controls commonly utilized in parallel industries. This section presents examples of how individual controls might be combined to treat wastewater streams prior to their ultimate disposal. The approaches considered in this section are not all inclusive but only serve to indicate how available controls may be applied to the subject wastes.

The controls selected in each example are largely determined by the ultimate disposal method being considered and the type of synthesis section utilized by the base plant. The specific waste stream quality required by each disposal method is uncertain and would be determined on a site-specific basis, but certain general requirements are associated with each, and these are incorporated in the integrated control examples.

Three ultimate disposal methods are considered: discharge to surface waters, surface impoundment, and deep well injection. In some cases, co-disposal of the wastewater with ash from the gasifier may also be a viable method (see Section 4.2.1.8). Potential sources of ash are incinerated dust from the gas cooling/dust removal blowdown, boiler bottom ash, and boiler fly ash. This ash is expected to sorb 20% water. Additionally, slag generated by the gasification section can sorb about 10% water. The total estimated capacity of wastewater that can be sorbed by ash is 6.7 m^3/hr. However, this capacity may vary greatly, depending primarily on the ash content of the feed coal, the slag/dust and ash partitioning during gasification, and the feasibility of resource recovery by incineration of gasifier dust.

It is not expected that the ash and slag generated by the gasifier would provide sufficient capacity to dispose of the entire wastewater volume. Co-disposal is therefore not considered further in this manual. However, while only single ultimate disposal methods are considered for each integrated control example in this section, several methods may be combined to satisfy the needed capacity. In this context co-disposal may be a viable option.

The type of synthesis operation utilized in the base plant affects the wastewater treatment approach required for the entire K-T plant. Both the F-T and Mobil M synthesis sections generate a waste stream that is heavily loaded with organics. Fuel grade methanol synthesis generates a much smaller volume of organic-loaded waste to the total wastewater stream, while crude methanol synthesis generates no waste stream from the synthesis operation. All other significant waste streams in the K-T facility contain principally inorganic constituents. Therefore, K-T plants that produce crude methanol generate, facility-wide, only waste streams having primarily inorganic constituents. Fuel grade methanol K-T plants generate only a small load of organics compared to the inorganics load of a combined wastewater, and F-T and Mobil M synthesis plants generate both heavily loaded organic and inorganic waste streams when gasification and synthesis wastes are combined. Somewhat different water pollution control approaches appear most advantageous for each of these three cases. Each case is considered separately in the following section.

4.2.4.1 Treatment of Waste Streams from Base Plants Utilizing F-T or Mobil M Synthesis

Both F-T and Mobil M synthesis operations generate a condensate having high concentrations of organics. These organics are relatively simple species including short chain hydrocarbons, ketones, and organic acids. It is expected that the F-T and Mobil M synthesis condensates will be highly amenable to biological oxidation: BOD was estimated to be 70% of COD. However, there are two problems in applying a conventional biological system to these waste streams. First, the concentration of organics exceeds the maximum normally handled by a suspended growth biological system such as activated sludge. Dilution of the waste stream by recycling the activated sludge effluent would require excessive pumping and increased capital costs. Other biological process reactors, such as fixed film reactors (trickling filters and others), could handle the high organic concentrations, but it is expected that following these processes, the organics concentration would remain relatively high so that an activated sludge process to effect more complete removal might still be advisable. Additionally, this approach does not address the second problem which is lack of growth nutrients. The subject waste stream does not contain nitrogen, phosphorus, sulfur, and trace amounts of other materials required for cell growth.

The waste streams generated by the gasifier section (Section 4.2.4) contain, among other species, ammonia and sulfide but no organics. By combining these waste streams with a synthesis condensate, the ammonia would supply most of the nitrogen and the sulfide would supply all of the sulfur required to support cell growth. The concentration of organics in the combined stream would be diluted to a level suitable for an activated sludge system. Characteristics of the individual waste streams from the gasifier section, the Mobil M condensate, and the combined streams are presented in Table 4-31. There are two cases of combined streams representing the two base plant designs for cyanide wash discussed in Section 3.3.4. Where cyanide is removed

TABLE 4-31. CHARACTERIZATION OF MAJOR STREAMS COMBINED FOR COMMON TREATMENT - MOBIL M SYNTHESIS CASE

Characteristic*	Gas Cooling/ Dust Removal Blowdown Stream 210	Compression Condensate Stream 211	Cyanide Wash Water Stream 215	Mobil M Condensate Stream 233	Composite	
					Base Plant Water-based†	Cyanide Wash Methanol-based‡
Flow (m^3/hr)	322	17.4	239	110	688	449
NH_3	156	735	--	--	92	140
CN^-	7	8.9	241	--	87	5
$S^=$	1	48.7	176	--	63	2.6
$S_2O_3^=$	103	6.3	--	--	48	74
$SO_3^=$	25	--	--	--	12	18
SCN^-	4	14	--	--	2.5	3
COD	--	--	--	14000	2200	3400
BOD_5	--	--	--	6860	1100	1700
Cl^-	2111	2200	--	--	1040	1600
TDS	4000	--	--	--	1900	2900

*All concentrations are mg/L.

†Combined streams: gas cooling/dust removal blowdown, compression condensate, cyanide wash water, and Mobil M condensate.

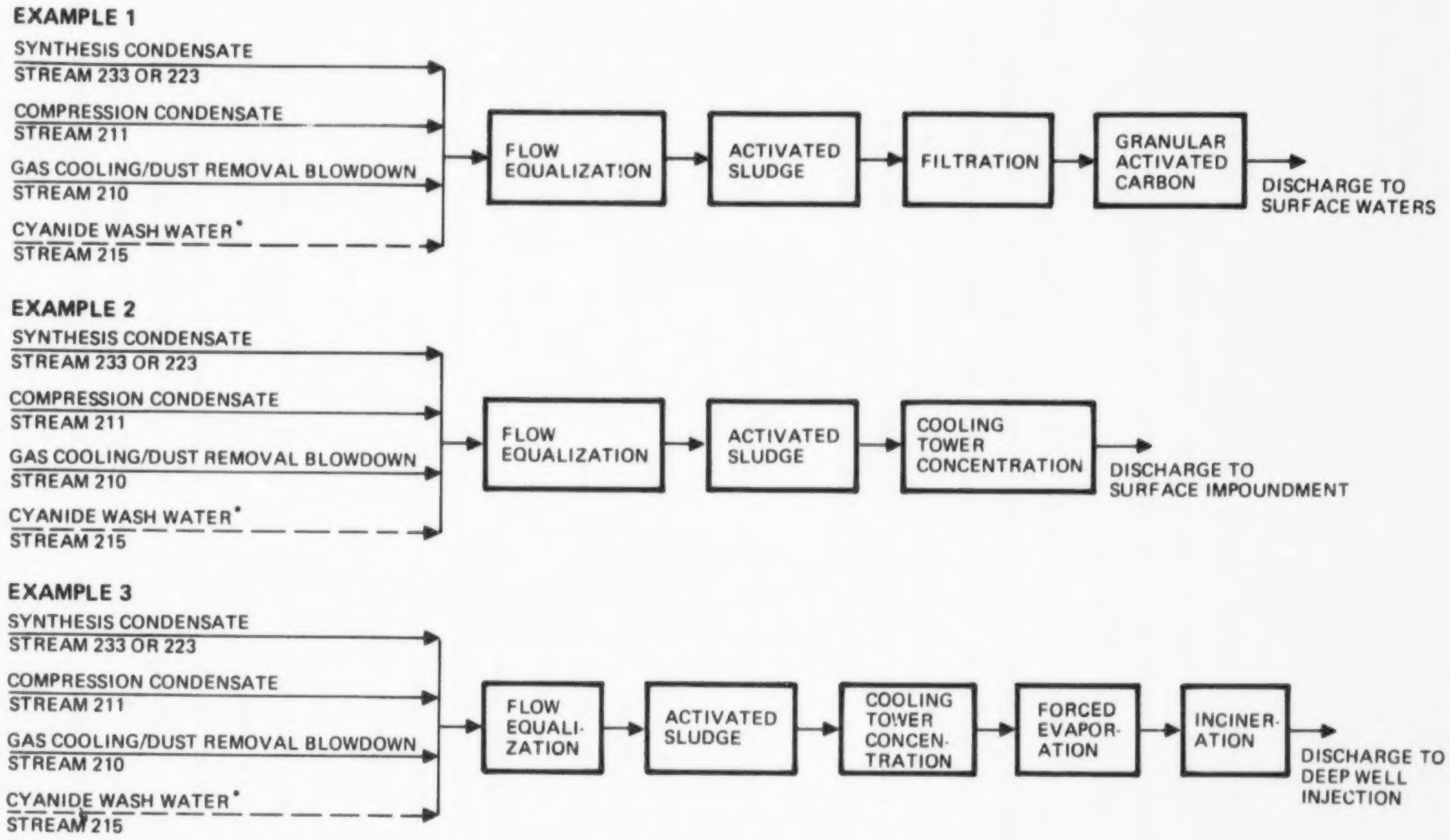
‡Combined streams: gas cooling/dust removal blowdown, compression condensate, and Mobil M condensate.

from the base plant by a water wash, a wastewater stream is generated contributing to a combined flow of 688 m^3/hr. Where cyanide is removed by a methanol-based wash essentially no wastewater is generated by this source, and the combined flow is 449 m^3/hr.

Presented in Figure 4-6 are three examples of integrated controls applicable to a composite waste stream consisting of the Mobil M condensate (Stream 233) combined with the wastewater streams from the gasifier section. Identical examples could be used for the F-T synthesis case with changes required only to reflect the different flow and organic loading of the F-T synthesis condensate. Neither performance nor cost characteristics would differ greatly.

A feature common to all integrated pollution control examples is flow equalization. Design performance of pollution control processes can be realized only when the waste stream characteristics vary gradually and within a generally narrow range. For some processes, particularly those based on the activity of microorganisms, equalization is especially critical. Under conditions of no more than slightly varying waste stream characteristics, microbial populations can usually be acclimated to both concentrations and types of chemical species that would otherwise not be degradable. If significant fluctuations in the input occur, there is no chance to acclimate the microbial culture, or worse, the entire system might fail requiring a complete, new start-up.

Certain waste streams in the K-T plant other than those from the gasifier or synthesis sections may also be routed to the equalization facility. These waste streams would contribute only minor flows and loadings to downstream controls. The exact requirements of the equalization facility are beyond the scope of this manual. Its design would take into consideration the variability of all waste stream inputs to be handled by the integrated controls.



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*This stream exists only for base plants where cyanide is removed from the raw gas by a water-based wash.

Figure 4-6. Integrated control examples - Mobil M or F-T synthesis case

Example 1. Integrated pollution controls in Example 1 of Figure 4-6 are an example of how the waste stream might be treated prior to ultimate disposal by direct discharge to surface waters. The controls are activated sludge, filtration, and granular activated carbon. The characteristics of the effluent from each control process are presented in Table 4-32 and the estimated characteristics of the wastewater stream discharged to surface waters by this illustrative example as well as by the other examples are presented subsequently in Table 4-35.

The activated sludge process would be designed primarily to remove organics. Since relatively simple organic species are involved, better than 95% removal is expected through one or more stages. Thiocyanate, thiosulfate, and sulfite would be concurrently oxidized.

Ammonia would be removed in the activated sludge process by being assimilated as new cell material. Because the nitrogen available in the composite flow is somewhat less than that required, extra nitrogen as ammonia would be added. All ammonia in excess of that required for cell growth would appear in the effluent. Therefore the concentration of ammonia in the effluent would depend on the degree of control exercised over its addition. While addition of ammonia representing its exact requirement is ideally possible, in practice the continuously varying organics concentration in the influent would necessitate excess ammonia addition.

Air or oxygen to support biological oxidation is supplied to the reactor under highly turbulent conditions. This maximizes the mass of oxygen transferred to the water, keeps the contaminants and microbial flocs dispersed throughout the reactor, but provides conditions that are highly favorable to stripping of volatile species. At the slightly alkaline reactor conditions needed for optimal microorganism growth, much of the sulfide would occur in its potentially volatile form, hydrogen sulfide (H_2S). While some of the sulfide would be oxidized by direct combination with oxygen and some biologically

TABLE 4-32. EXAMPLE 1 - MATERIAL FLOW FOR MOBIL M SYNTHESIS BASE PLANT INTEGRATED CONTROLS (FIGURE 4-6)

	Composite		Activated Sludge		Filtration		Granular Activated Carbon	
Base Plant Cyanide Wash:	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Characteristic*								
Flow (m^3/hr)	688	449	688	449	688	449	688	449
NH_3	92	140	10	10	10	10	10	10
CN^-	87	5	9-35	1	9-35	1	9-35	1
$S^=$	63	2.6	<1	<1	<1	<1	<1	<1
$S_2O_3^=$	48	74	<1	<1	<1	<1	<1	<1
$SO_3^=$	12	18	<1	<1	<1	<1	<1	<1
SCN^-	2.5	3	<1	<1	<1	<1	<1	<1
COD	2200	3400	680	1060	680	1060	70	100
BOD_5	1100	1700	35	42	35	42	21	28
Cl^-	1040	1600	1040	1600	1040	1600	1040	1600
TDS	1900	2900	1900	2900	1900	2900	1900	2900
TSS	--	--	30	30	<10	<10	<10	<10

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

oxidized, the greatest fraction would probably be stripped from solution. Since this hydrogen sulfide is transferred to the atmosphere at near ground level, even low level emissions may cause odor problems.

Stripping may also occur with cyanide. At the near neutral conditions found in the reactor, nearly all the cyanide would exist as the potentially volatile hydrogen cyanide species (HCN). It is not certain how much cyanide would be volatilized and how much would be oxidized biologically. For base plant designs utilizing a methanol-based cyanide wash, both the cyanide and sulfide concentrations in the composite wastewater stream would be much lower than in the water-based case resulting in less potential for stripping. In either case, if stripping of volatile species (Stream 416) is identified as a problem, the activated sludge reactor could be covered. Air circulated through the overhead space could be covered. Air circulated through the overhead space could be routed to the boiler or to an incinerator.

Cyanide can be oxidized or otherwise removed by activated sludge systems where the cyanide occurs as part of a matrix of predominatly organic species. Greater than 90% cyanide removal has been recorded in the literature for carefully controlled laboratory-scale reactors. The exact cyanide removal that could actually be realized in an operating system is highly uncertain. For purposes of this manual, 60 to 90% removal through one or more stages of activated sludge has been assumed. If this removal is not sufficient or is determined to be unattainable, much of the cyanide can be converted to the easily degradable thiocyanate species by adding polysulfide prior to the activated sludge process. Polysulfide addition is not expected to be required in this application and therefore is not included in cost or performance estimates. Details of polysulfide addition are presented in Section 4.2.1 and 4.2.3.

The activated sludge process is followed by filtration to remove suspended solids, especially cells that escape the activated sludge clarifier.

Although after filtration, the waste stream could possibly be discharged to surface waters, it is expected that residual/refractory organics that could not be oxidized by the activated sludge process will remain. Where it is determined that these need to be removed, a granular activated carbon system could be added. Granular activated carbon would also remove some trace metals if these are present.

Example 2. Integrated pollution controls in Example 2 are illustrative of those that might be used to treat the waste stream prior to ultimate disposal by surface impoundment. Estimated characteristics of the wastewater stream discharged to surface impoundment are presented in Table 4-35. The controls are activated sludge and cooling tower concentration. Effluent characteristics for each control are presented in Table 4-33.

All aspects of the activated sludge process are identical to those presented in Example 1. Following treatment by activated sludge, the waste stream could possibly be suitable for discharge to a surface impoundment; however, the capital requirements of surface impoundment can be decreased greatly by reducing the volume of water to be held. The cooling tower would be used for this purpose with the waste stream combined with raw water (or recycle water) to supply the cooling tower makeup.

Cooling tower concentration is expected to be very attractive since this system is a capital requirement of the base plant regardless of its source of makeup water. Problems associated with using low quality makeup water to the cooling tower have been discussed elsewhere (Section 4.2.1). Fouling by biological solids escaping the activated sludge process or growing within the tower can be controlled by biocides. Alternatively, the biological solids as well as any other suspended material can be removed by filtering the activated sludge effluent. Where scaling such as by calcium sulfate or corrision, particularly by chloride, are problems, various pretreatments would be needed. However, at some point the cost of additional treatment to prepare the waste stream suitable for cooling tower concentration would exceed any benefit of

TABLE 4-33. EXAMPLE 2 - MATERIAL FLOW FOR MOBIL M SYNTHESIS BASE PLANT INTEGRATED CONTROLS (FIGURE 4-6)

	Composite		Activated Sludge		Cooling Tower Concentration	
Base Plant Cyanide Wash:	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Characteristic*						
Flow (m^3/hr)	688	449	688	449	180	180
NH_3	92	140	10	10	38[†]	25[†]
CN^-	87	5	9-35	1	34-130[‡]	2[‡]
$S^=$	63	2.6	<1	<1	<1	<1
$S_2O_3^=$	48	74	<1	<1	4	2
$SO_3^=$	12	18	<1	<1	4	2
SCN^-	2.5	3	<1	<1	4	2
COD	2200	3400	680	1060	2600	2650
BOD_5	1100	1700	35	42	130	105
Cl^-	1040	1600	1040	1600	3900	4000
TDS	1900	2900	1900	2900	7200	7200
TSS	--	--	30	30	110	75

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

[†] No ammonia volatilization is assumed.

[‡] Loss by volatilization/biological oxidation uncertain - no losses assumed.

reducing its volume for downstream handling. The feasibility of this system will, therefore, have to be determined on an individual case basis once the compositions of the waste streams are known with some certainty.

Blowdown from the cooling tower will contain the original constituents in the makeup stream but concentrated by a factor that is the ratio of makeup flow to blowdown. Some losses will result from volatilization or entrainment in the drift (Stream 419), but the exact amounts are uncertain and must be evaluated on an individual case basis. The blowdown stream would be routed to ultimate disposal by surface impoundment.

Example 3. Integrated pollution controls in Example 3 of Figure 4-6 are illustrative of those that might be utilized prior to ultimate disposal of the wastewater stream by a combination of recycle and deep well injection. Estimated characteristics of the wastewater stream that is deep well injected are summarized in Table 4-35. The controls are activated sludge, cooling tower concentration, forced evaporation, and incineration. Effluent characteristics for each control process are presented in Table 4-34.

Example 3 differs from Example 2 only in the handling of the cooling tower blowdown. The blowdown is routed to forced evaporation where the original waste stream constituents are concentrated into a low flow stream. Certain characteristics of the waste stream may limit the usability of forced evaporation; these considerations have been addressed in Section 4.2.1. The forced evaporation overhead is virtually free of contaminants and would be recycled for use as high quality makeup water within the facility. The forced evaporation concentrate would be deep well injected (or alternatively surface impounded) after it has been incinerated to remove high concentrations of organics that would otherwise foul the injection formation.

Costs for integrated pollution controls shown in Figure 4-6 are presented in Table 4-36. All costs depend on the type of cyanide wash used in the base plant design. For each integrated example, costs are presented in total

TABLE 4-34. EXAMPLE 3 - MATERIAL FLOW FOR MOBIL M SYNTHESIS BASE PLANT INTEGRATED CONTROLS (FIGURE 4-6)

	Composite		Activated Sludge		Cooling Tower Concentration		Forced Evaporation		Incineration	
Base Plant Cyanide Wash:	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Characteristic*										
Flow (m^3/hr)	688	449	688	449	180	180	18	18	18	18
NH_3	92	140	10	10	38	25	380	250	0.2	0.1
CN^-	87	5	9-35	1	34-130	2	340-1300	20	0.3-1	0.02
$S^=$	63	2.6	<1	<1	<1	<1	<1	<1	<1	<1
$S_2O_3^=$	48	74	<1	<1	4	2	40	20	40	20
$SO_3^=$	12	18	<1	<1	4	2	40	20	40	20
SCN^-	2.5	3	<1	<1	4	2	40	20	0.04	0.02
COD	2200	3400	680	1060	2600	2650	26000	26500	26	26
BOD_5	1100	1700	35	42	130	105	1300	1050	1	1
Cl^-	1040	1600	1040	1600	3900	4000	39000	40000	39000	40000
TDS	1900	2900	1900	2900	7200	7200	72000	72000	72000	72000
TSS	--	--	30	30	110	75	1100	750	--	--

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

TABLE 4-35. ESTIMATED CHARACTERISTICS OF WASTEWATER STREAMS DISCHARGED TO ULTIMATE DISPOSAL - MOBIL M SYNTHESIS CASE

Integrated Controls:	Example 1		Example 2		Example 3	
Ultimate Disposal:	Surface Waters		Surface Impoundment		Deep Well Injection	
Base Plant Cyanide Wash:	Water	Methanol	Water	Methanol	Water	Methanol
Characteristic*						
Flow (m^3/hr)	688	449	180	180	18	18
NH_3	10	10	38	25	0.2	0.1
CN^-	9-35	1	34-130	2	0.3-1	0.02
$S^=$	<1	<1	<1	<1	<1	<1
$S_2O_3^=$	<1	<1	4	2	40	20
$SO_3^=$	<1	<1	4	2	40	20
SCN^-	<1	<1	4	2	0.04	0.02
COD	70	100	2600	2650	26	26
BOD_5	21	28	130	105	1	1
Cl^-	1040	1600	3900	4000	39000	40000
TDS	1900	2900	7200	7200	72000	72000
TSS	<10	<10	110	75	--	--

*All concentrations are mg/L.

TABLE 4-36. COSTS OF INTEGRATED CONTROL EXAMPLES - MOBIL M SYNTHESIS CASE

Integrated Control Example	Ultimate Disposal Technique	Total Capital Investment*		Total Annualized Cost*		% of Base Plant Capital Cost	
		Base Plant Cyanide Wash					
		Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Example 1	Surface waters	19.5	19.1	6.5	5.7	1.6	1.6
Controls: Activated Sludge		18.3	18.3	3.9	3.9		
Filtration		1.2	0.78	2.6	1.8		
Additional Control: Granular Activated Carbon		3.1	3.0	1.5	1.6		
Example 2	Surface Impoundment	26.6	26.6	5.6	5.6	2.2	2.2
Controls: Activated Sludge		18.3	18.3	3.9	3.9		
Surface Impoundment		8.3	8.3	1.7	1.7		
Example 3	Deep well injection	39.4	39.4	10.3	10.3	3.2	3.2
Controls: Activated Sludge		18.3	18.3	3.9	3.9		
Forced Evaporation		13.7	13.7	3.5	3.5		
Incineration		4.8	4.8	2.3	2.3		
Deep Well Injection		2.6	2.6	0.56	0.56		

*Million dollars

capital investment and total annualized cost for both individual controls and the entire integrated system; and percent of base plant cost for the entire integrated system. Costs of additional controls that are possibly applicable have also been included.

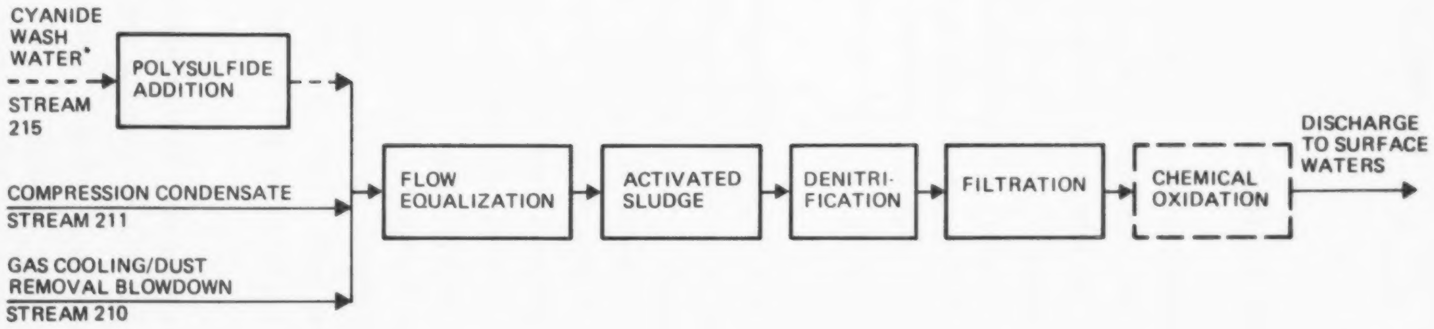
4.2.4.2 Treatment of Waste Streams from Base Plants Producing Crude Methanol

The integrated wastewater control examples presented thus far have been designed to treat a highly organic waste stream from a synthesis section (F-T or Mobil M) combined with strictly inorganic waste streams from the gasifier section. The resulting composite flow is highly amenable to treatment by a conventional activated sludge process; the high organic concentrations are diluted to an appropriate level for biological oxidation, and the inorganic species from the gasifier wastewaters are biological oxidized, utilized as growth nutrients and thereby assimilated as new cell material, or are otherwise removed.

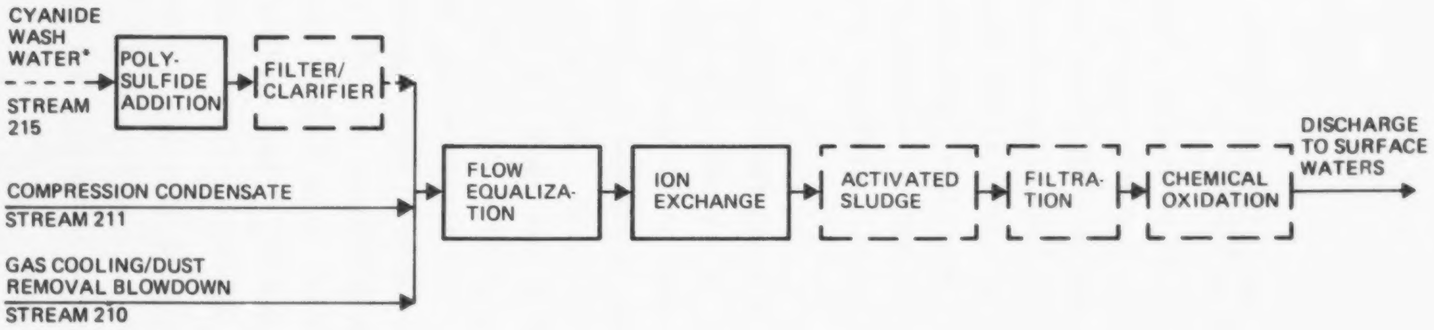
This water management strategy is not usable for K-T facilities where crude methanol is produced since no high volume waste stream with organics equivalent to that generated by F-T or Mobil M synthesis would exist. The composite waste stream would consist exclusively of inorganic species, particularly ammonia, cyanide, thiocyante, and a variety of reduced sulfur species. There is no known precedent for treating a waste stream having significant concentrations of each of the cited species. Due to these unique characteristics, some novel treatment approaches are worth considering. Two examples of integrated controls are presented in Figure 4-7 for cases where ultimate disposal is by discharge to surface waters, and examples for cases where ultimate disposal is by surface impoundment or deep well injection are presented in Figure 4-8. Each addresses the two base plant designs of cyanide removal by a water or methanol wash.

Cyanide can be partially destroyed in biox processes. Microorganisms in an activated sludge process can be acclimated to oxidize cyanide but only where the cyanide is part of a larger matrix dominated by biodegradable organics. However, cyanide can be removed from stricly inorganic wastewater streams by converting it to thiocyanate then oxidizing the thiocyanate.

EXAMPLE 4



EXAMPLE 5



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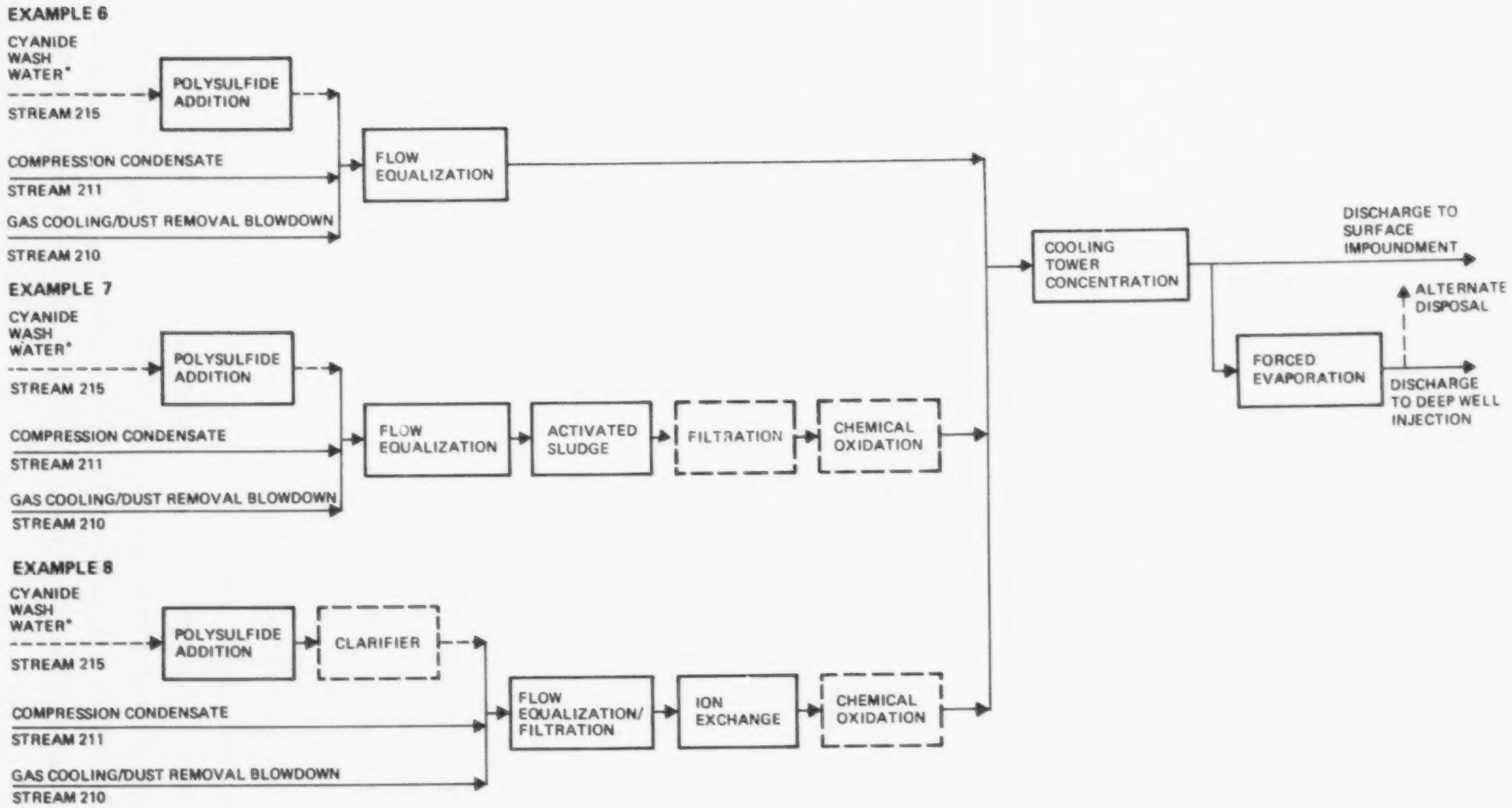
*This stream exists only for base plants where cyanide is removed from the raw gas by a water-based wash.

Figure 4-7. Integrated control examples for base plants producing crude methanol - discharge to surface waters



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*This stream exists only for base plants where cyanide is removed from the raw gas by a water-based wash.

Figure 4-8. Integrated control examples for base plants producing crude methanol - discharge to surface impoundment or deep well injection

Laboratory scale studies have demonstrated that thiocyanate can be biologically oxidized even where it and ammonia are the only usable growth substrates for the microorganisms. Sulfur, when added as polysulfide, would drive the conversion.

Assuming excess polysulfide addition, the influent and desired effluent concentrations of cyanide determine the reaction time required for the thiocyanate conversion. In general, the effluent concentration is more critical since large increases in reaction time are required to achieve small decreases in the effluent cyanide concentration at effluent levels less than about 10 mg/L cyanide. Therefore, polysulfide addition does not appear to be economical for waste streams such as the gas cooling/dust removal blowdown (Stream 210) and the compression condensate (Stream 211) having less than 10 mg/L cyanide. However, both the cyanide concentration and loading of the cyanide wash water (Stream 215) are expected to be well over an order of magnitude greater than that of the other two streams. By treating the cyanide wash water with polysulfide separately, the reaction can be accomplished under kinetically more favorable conditions than if all three streams had first been combined. Since the cyanide wash water would then be combined with the gas-cooling/dust removal blowdown and compression condensate and since both of these streams contain cyanide at about the 10 mg/L level, the cyanide wash water would be treated by polysulfide addition to a corresponding level. If it is desired to decrease the cyanide concentration in the composite stream to a lower level, downstream controls could be applied.

For each integrated control example (Figures 4-7 and 4-8) where cyanide is removed from the base plant by a water wash, polysulfide addition would be desirable as a pretreatment step. Characteristics of the cyanide wash water (Stream 215) before and after polysulfide addition are presented in Table 4-37. The characteristics of the compression condensate (Stream 211) and of the gas cooling/dust removal blowdown (Stream 210) are also presented in Table 4-37

TABLE 4-37. CHARACTERIZATION OF MAJOR STREAMS TO BE COMBINED FOR TREATMENT - CRUDE METHANOL PRODUCTION CASE

					Composite	
Characteristic*	Cyanide Wash Water Stream 215	Cyanide Wash Pretreated with Polysulfide	Gas Cooling/ Dust Removal Blowdown Stream 210	Compression Condensate Stream 211	Base Plant Water-Based†	Cyanide Wash Methanol-Based‡
Flow (m^3/hr)	239	239	322	17.4	578	339
NH_3	--	360	156	735	260	190
CN^-	241	8	7	8.9	7.5	7
$S^=$	176	<1	1	48.7	2	3.5
$S_2O_3^=$	--	--	103	6.3	58	98
$SO_3^=$	--	--	25	--	14	24
SCN^-	--	495	4	14	210	4.5
Cl^-	--	--	2111	2200	1200	2100
TDS	--	--	4000	--	2200	3800

*All concentrations are mg/L.

†Combined streams: cyanide wash water pretreated by polysulfide addition, gas cooling/dust removal blowdown, and compression condensate.

‡Combined streams: gas cooling/dust removal blowdown and compression condensate.

as are the characteristics of the composite flows from base plants using a water-based or methanol-based cyanide wash.

As was the case for integrated pollution controls for a base plant having a Mobil M or F-T synthesis section, each of the examples (Figures 4-7 and 4-8) for the subject crude methanol production case would use flow equalization.

Example 4, Figure 4-7. Integrated pollution controls in Example 4 of Figure 4-7 are illustrative of those that might be utilized prior to ultimate disposal of the composite wastewater stream by direct discharge to surface waters. The controls are activated sludge, denitrification, and filtration. Characteristics of the effluent from each control are summarized in Table 4-38, and the estimated characteristics of the wastewater stream discharged to surface waters by this illustrative example as well as by the other examples presented in Figures 4-7 and 4-8 are presented in Table 4-43.

In the activated sludge process, both ammonia and thiocyanate would be oxidized. An oxidation product of each of these species is nitrate; it would be biologically reduced to molecular nitrogen in a following denitrification reactor.

As discussed for Example 4 of Figure 4-6, it may be advisable to cover and vent to an incinerator both the polysulfide and the nitrification reactors to prevent loss of the potentially volatile hydrogen sulfide and hydrogen cyanide species. Following denitrification, loss of volatile species is not expected to present problems.

Following deniitrification, the waste stream is filtered to remove suspended solids that escape the denitrification clarifier. At this point, the waste stream could possibly be discharged to surface waters. If additional treatment is desirable, particularly to further reduce the cyanide concentration, chemical oxidation can be included.

Example 5, Figure 4-7. Integrated pollution controls in Example 5 of Figure 4-7 are also aimed toward ultimate disposal of the composite wastewater

TABLE 4-38. EXAMPLE 4 - MATERIAL FLOW FOR CRUDE METHANOL PRODUCTION BASE PLANT INTEGRATED CONTROLS (FIGURE 4-7)

	Composite		Nitrification		Denitrification		Filtration	
Base Plant Cyanide Wash:	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Characteristic*								
Flow (m^3/hr)	578	339	578	339	578	339	578	339
NH_3	260	190	10	7	10	7	8	6
CN^-	7.5	7	7.5	7	7.5	7	7.5	7
$S^=$	2	3.5	<1	<1	<1	<1	<1	<1
$S_2O_3^=$	58	98	<1	<1	<1	<1	<1	<1
$SO_3^=$	14	24	<1	<1	<1	<1	<1	<1
SCN^-	210	4.5	<1	<1	<1	<1	<1	<1
Cl^-	1200	2100	1200	2100	1200	2100	1200	2100
TDS	2200	3800	>2200	>3800	>2200	>3800	>2200	>3800
NO_3^--N	<1	<1	245	140	24	15	24	15
TSS	<50	<50	<50	<50	30	30	<10	<10

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

TABLE 4-39. EXAMPLE 5 - MATERIAL FLOW FOR CRUDE METHANOL PRODUCTION BASE PLANT INTEGRATED CONTROLS (FIGURE 4-7)

	Composite		Ion Exchange		Activated Sludge		Filtration	
Base Plant Cyanide Wash:	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Characteristic*								
Flow (m^3/hr)	578	339	578	339	578	--	578	--
NH_3	260	190	12	12	12	--	12	--
CN^-	7.5	7	7.5	7	7.5	--	7.5	--
$S^=$	2	3.5	2	3.5	<1	--	<1	--
$S_2O_3^=$	58	98	58	98	<1	--	<1	--
$SO_3^=$	14	24	14	24	<1	--	<1	--
SCN^-	210	4.5	210	4.5	<1	--	<1	--
Cl^-	1200	2100	>1200	>2100	>1200	--	>1200	--
TDS	2200	3800	>2200	>3800	>2200	--	>2200	--
NO_3^--N	--	--	--	--	60	--	60	--
TSS	--	--	--	--	30	--	<10	--

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

stream by direct discharge to surface waters. Estimated characteristics of the wastewater stream discharged to surface waters are presented in Table 4-43. For the methanol-based cyanide wash case, ion exchange is the primary control. Activated sludge, filtration, and chemical oxidation can also be included if additional treatment is desired. Estimated performance of individual controls is presented in Table 4-39.

As is the case for all examples in Figure 4-7 and 4-8, where the cyanide wash water occurs, it is pretreated by polysulfide addition. This reaction must be completed at alkaline conditions, but downstream pollution control processes require near neutral or only slightly alkaline conditions. If the acidity of the streams with which the cyanide wash would be combined is not sufficient to produce a composite flow having a stable, near neutral condition, the cyanide wash should be first neutralized by acid addition. In any case, under neutral conditions, residual polysulfide may precipitate. This precipitate is not expected to cause significant problems with the nitrification process of Example 4, but for the following ion exchange process of this example, plugging and fouling would result. For purposes of this manual, the cyanide wash is assumed to be neutralized following polysulfide addition so that, if needed, a filter or clarifier can be dedicated separately to this stream.

Ion exchange using an exchange resin of clinoptilolite would remove ammonium ions from the waste stream and replace them with sodium ions. All known experience to date with this system is associated with removing ammonia from low-strength municipal wastewaters. However, preliminary, EPA supported studies strongly suggest that the process would be equally feasible for a waste stream having the characteristics of the K-T composite stream.

For base plant cases using a methanol-based cyanide wash, the composite wastewater stream may be suitable for discharge to surface waters following ion exchange. If additional treatment is determined necessary, chemical oxidation can be included. For the case of the water-based cyanide wash, a biological treatment process followed by a filter would be included following ion exchange to oxidize the thiocyanate that had been converted from cyanide by upstream polysulfide addition.

Example 6, Figure 4-8. Examples of integrated controls presented in Figure 4-8 are illustrative of cases where the ultimate discharge technique is either surface impoundment or complete recycle with deep well injection. Estimated characteristics of the wastewater stream discharged to surface impoundment or deep well injected are presented in Table 4-43 for each of the three examples. Each example utilizes cooling tower concentration to reduce the volume of water to be handled for disposal. The cooling tower blowdown would be disposed of by surface impoundment, or if recovery of water for reuse is desired, the blowdown would be routed to forced evaporation. The forced evaporation overhead would contain only trace amounts of contaminants and would be recycled for use as makeup water within the facility. Concentrate from this process would be disposed of by deep well injection or surface impoundment.

Since cooling tower concentration is common to each of the examples in Figure 4-8, upstream control processes are determined by the requirements of this step. Problems with scaling, fouling, and corrosion that may limit the feasibility of cooling tower concentration have been discussed in Section 4.2.1. It has been assumed that no extraordinary pretreatments would be required to correct these problems. Control processes are assumed only to remove volatile species that may be lost to the atmosphere during the concentration process.

In general, it is not certain how much of a particular volatile species would be lost to the atmosphere during cooling tower concentration. Additionally, different losses may be acceptable at different locations. It is assumed, however, that the concentration of cyanide in the cooling tower makeup would have to be at low levels since at the expected pH operating range nearly all the cyanide would exist as the potentially volatile hydrogen cyanide species. Therefore, all cases where cyanide is removed from the base plant by a water wash, polysulfide addition is included as a pretreatment step.

Example 6 represents a case where no treatment of the composite wastewater stream is included prior to its being used as cooling tower makeup. In some facilities, this approach might be feasible; however, this approach is not very likely due to expected volatilization of ammonia and sulfide in the cooling tower. Estimated characteristics of the composite wastewater stream following cooling tower concentration and forced evaporation are presented in Table 4-40.

Example 7, Figure 4-8. It is very likely that the composite wastewater stream would be treated for removal of volatile species prior to being routed to cooling tower makeup. Example 7 utilizes activated sludge. Estimated characteristics of the subject wastewater stream through all control processes are presented in Table 4-41. All other details are identical to those presented in Example 4 of Figure 4-7. Where it is determined that even higher quality makeup water is desired, filtration can be added to remove suspended solids and chemical oxidation added to oxidize ammonia, cyanide, and other remaining reduced species.

Example 8, Figure 4-8. Like Example 7, Example 8 prepares the subject wastewater stream for use as makeup to the cooling tower. The control process for this example is ion exchange. Details are identical to those presented in Example 5 of Figure 4-7. Where additional treatment is needed, chemical oxidation could be added. Characteristics of the subject wastewater stream through all control processes are presented in Table 4-42.

Costs for integrated pollution controls for each example presented in Figures 4-7 and 4-8 are summarized in Table 4-44. All costs depend on the type of cyandie wash used in the base plant design. For each integrated example, costs are presented as total capital investment and total annualized cost for both individual controls and the entire integrated system; and as a percentage of base plant cost for the entire integrated system. Costs of additional controls that are possibly applicable are also presented.

TABLE 4-40. EXAMPLE 6 - MATERIAL FLOW FOR CRUDE METHANOL PRODUCTION BASE PLANT INTEGRATED CONTROLS (FIGURE 4-8)

	Composite		Cooling Tower Concentration		Forced Evaporation†	
Base Plant Cyanide Wash:	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Characteristic*						
Flow (m^3/hr)	578	339	161	161	16	16
NH_3	260	190	933	400	9330	4000
CN^-	7.5	7	27	15	270	150
$S^=$	2	3.5	<1	<1	<1	<1
$S_2O_3^=$	58	98	205	205	2050	2050
$SO_3^=$	14	24	50	50	500	500
SCN^-	210	4.5	740	8	7400	80
Cl^-	1200	2100	4500	4400	45000	44000
TDS	2200	3800	7900	8000	79000	80000

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

†Required for recycle only.

TABLE 4-41. EXAMPLE 7 - MATERIAL FLOW FOR CRUDE METHANOL PRODUCTION BASE PLANT INTEGRATED CONTROLS (FIGURE 4-8)

Base Plant	Composite		Activated Sludge		Cooling Tower Concentration		Forced Evaporation†	
Cyanide Wash:	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Characteristic*								
Flow (m^3/hr)	578	339	578	339	161	161	16	16
NH_3	260	190	10	7	36	15	360	150
CN^-	7.5	7	7.5	7	27	15	270	150
$S^=$	2	3.5	<1	<1	<1	<1	<1	<1
$S_2O_3^=$	58	98	<1	<1	4	2	40	20
$SO_3^=$	14	24	<1	<1	4	2	40	20
SCN^-	210	4.5	<1	<1	4	2	40	20
Cl^-	1200	2100	1200	2100	4300	4400	43000	44000
TDS	2200	3800	>2200	>3800	>7900	>8000	>79000	>80000
NO_3^--N	-	-	245	140	880	300	8800	3000
TSS	-	-	30	30	110	60	1100	600

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

†Required for recycle only.

TABLE 4-42. EXAMPLE 8 - MATERIAL FLOW FOR CRUDE METHANOL PRODUCTION BASE PLANT INTEGRATED CONTROLS (FIGURE 4-8)

Base Plant	Composite		Ion Exchange		Cooling Tower Concentration		Forced Evaporation†	
Cyanide Wash:	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Characteristic*								
Flow (m^3/hr)	578	339	578	339	161	161	16	16
NH_3	260	190	12	12	43	25	430	250
CN^-	7.5	7	7.5	7	27	15	270	150
$S^=$	2	3.5	2	3.5	<1	<1	<1	<1
$S_2O_3^=$	58	98	57	98	205	205	2050	2050
$SO_3^=$	14	24	14	24	50	50	500	500
SCN^-	210	4.5	210	4.5	740	8	7400	80
Cl^-	1200	2100	>1200	>2100	>4300	>4400	>43000	>45000
TDS	2200	3800	>2200	>3800	>7900	>8000	>79000	>80000

*All concentrations are mg/L and reflect published data and engineering estimates. Detailed performance data and references are contained in the Control Technology Appendices.

†Required for recycle only.

TABLE 4-43. ESTIMATED CHARACTERISTICS OF WASTEWATER STREAMS DISCHARGED TO ULTIMATE DISPOSAL - CRUDE METHANOL PRODUCTION CASE

Integrated Controls: Figure:	Example 4 4-7		Example 5 4-7		Example 6 4-8		Example 6 4-8		Example 7 4-8		Example 7 4-8		Example 8 4-8		Example 8 4-8	
Ultimate Disposal:	Surface Waters		Surface Waters		Surface Impoundment		Deep Well Injection		Surface Impoundment		Deep Well Injection		Surface Impoundment		Deep Well Injection	
Base Plant Cyanide Wash:	Water	Methanol	Water	Methanol	Water	Methanol	Water	Methanol	Water	Methanol	Water	Methanol	Water	Methanol	Water	Methanol
Characteristic*																
Flow (m^3/hr)	578	339	578	339	161	161	16	16	161	161	16	16	161	161	16	16
NH_3	8	6	12	12	933	400	9330	4000	36	15	360	150	43	25	430	250
CN^-	7.5	7	7.5	7	27	15	270	150	27	15	270	150	27	15	270	150
$S^=$	<1	<1	<1	3.5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
$S_2O_3^=$	<1	<1	<1	98	205	205	2050	2050	4	2	40	20	205	205	2050	2050
$SO_3^=$	<1	<1	<1	24	50	50	500	500	4	2	40	20	50	50	500	500
SCN^-	<1	<1	<1	4.5	740	8	7400	80	4	2	40	20	740	8	7400	80
Cl^-	1200	2100	>1200	>2100	4500	4400	45000	44000	4300	4400	43000	44000	>4300	>4400	>43000	>45000
TDS	>2200	>3800	>2200	>3800	7900	8000	79000	80000	>7900	>8000	>79000	>80000	>7900	>8000	>79000	>80000
NO_3^--N	24	15	60	--	--	--	--	--	880	300	8800	3000	--	--	--	--
TSS	<10	<10	<10	--	--	--	--	--	110	60	1100	600	--	--	--	--

*All concentrations are mg/L.

TABLE 4-44. COSTS OF INTEGRATED CONTROL EXAMPLES - CRUDE METHANOL PRODUCTION CASE

Integrated Control Example	Ultimate Disposal Method	Total Capital Investment*		Total Annualized Cost*		Percent of Base Plant Cost	
				Base Plant Cyanide Wash			
		Water-based	Methanol-based	Water-based	Methanol-based	Water-based	Methanol-based
Example 4, Figure 4-7	Surface Waters	19.8	10.5	5.8	2.6	1.8	0.9
Controls: Polysulfide		0.13	-	0.73	-		
Activated Sludge		12.6	6.7	2.7	1.5		
Denitrification		6.1	3.2	2.2	0.98		
Filtration		1.0	0.59	0.22	0.15		
Additional							
Control: Chemical Oxidation		0.72	0.16	0.23	0.12		
Example 5, Figure 4-7	Surface Waters	18.8	8.3	5.6	1.8	1.7	0.7
Controls: Polysulfide		0.13	-	0.73	-		
Ion Exchange		12.9	8.3	3.5	1.8		
Activated Sludge		4.8	-	1.1	-		
Filtration		1.0	-	0.22	-		
Additional							
Controls: Filtration		0.42	-	0.11	-		
Chemical Oxidation		0.72	0.16	0.23	0.35		
Example 6, Figure 4-8	Surface Impoundment	8.4	8.3	2.4	1.7	0.8	0.8
	Deep Well Injection	16.4	16.3	4.8	4.1	1.5	1.5
Controls: Polysulfide		0.13	-	0.73	-		
Surface Impoundment		8.3	8.3	1.7	1.7		
Forced Evaporation		13.7	13.7	3.5	3.5		
Deep Well Injection		2.6	2.6	0.56	0.56		
Example 7, Figure 4-8	Surface Impoundment	21.0	15.0	5.1	3.2	1.9	1.4
	Deep Well Injection	29.0	23.0	7.5	5.6	2.5	2.0
Controls: Polysulfide		0.13	-	0.73	-		
Activated Sludge		12.6	6.7	2.7	1.5		
Surface Impoundment		8.3	8.3	1.7	1.7		
Forced Evaporation		13.7	13.7	3.5	3.5		
Deep Well Injection		2.6	2.6	0.56	0.56		
Additional							
Controls: Filtration		1.0	0.59	0.22	0.15		
Chemical Oxidation		0.72	0.16	0.23	0.12		
Example 8, Figure 4-8	Surface Impoundment	21.4	16.6	5.9	3.5	1.9	1.5
	Deep Well Injection	29.3	24.6	8.3	5.9	2.6	2.2
Controls: Polysulfide		0.13	-	0.73	-		
Ion Exchange		12.9	8.3	3.5	1.8		
Surface Impoundment		8.3	8.3	1.7	1.7		
Forced Evaporation		13.7	13.7	3.5	3.5		
Deep Well Injection		2.6	2.6	0.56	0.56		
Additional							
Controls: Filtration		0.42	-	0.11	-		
Chemical Oxidation		0.72	0.16	0.23	0.35		

*Million dollars

4.2.4.3 Treatment of Waste Streams from Base Plants Producing Fuel Grade Methanol

For base plant cases where fuel grade methanol is produced, an organic waste stream would be generated by the methanol distillation step. However, when this waste stream is combined with gasification wastewaters, the total stream would probably not contain a high enough organic loading to be handled by integrated controls analogous to those of the F-T and Mobil M synthesis cases. Instead, controls would be similar to those in the crude methanol case with some modifications. Appropriate modifications of applicable integrated control examples of Figures 4-7 and 4-8 are considered in this section.

Example 4, Figure 4-7. The integrated controls presented in Example 4 of Figure 4-7 would be applicable to base plant cases where fuel grade methanol is produced. For base plant designs where cyanide is removed from the raw gas by a water-based wash, the methanol distillation condensate (Stream 229) could be routed to the denitrification reactor to provide the source of organics for reduction of nitrate to molecular nitrogen. For base plant designs where cyanide is removed by a methanol-based wash, the organic loading of the methanol distillation condensate would exceed that needed by the denitrification reactor. The excess could be routed upstream to the nitrification reactor. In either case, capital costs are expected to change by little, but annualized costs would decrease by about $814,000 and $296,000 for the two respective cases.

Example 5, Figure 4-7. Example 5 of Figure 4-7 would be applicable to plants producing fuel grade methanol, but unlike the crude methanol case discussed earlier, the activated sludge process would be needed for both the water- and methanol-based cyanide wash cases. The methanol distillation condensate (Stream 229) would be routed to the activated sludge process, and most of the nutrient requirements of this biological system would be met by bleeding ammonia through the upstream, clinoptilolite-based ion exchange process.

Example 6, Figure 4-8. For Example 6 of Figure 4-8 to be applicable to fuel grade methanol plants, an activated sludge system would probably have to be added. This example would then be essentially identical to the following, Example 7.

Example 7, Figure 4-8. Example 7 of Figure 4-8 would be directly applicable to base plants producing fuel grade methanol. The methanol distillation condensate (Stream 229) could be routed to the activated sludge reactor. Capital and annualized costs would be affected only slightly.

Example 8, Figure 4-8. To be applicable to base plants producing fuel grade methanol, an activated sludge reactor would be added to Example 8 of Figure 4-8 to follow the ion exchange process. The methanol distillation condensate (Stream 229) could be routed to the activated sludge reactor, and most nutrient requirements for this system would be met by bleeding some ammonia through the upstream ion exchange process. Capital and annualized cost changes would be reflected by the requirements of the added activated sludge process.

4.3 SOLID WASTE MANAGEMENT

Many solid waste streams including ashes and sludges are generated in a K-T based indirect liquefaction facility. The available control techniques that are applicable to these streams are identified and evaluated in this section. In comparison with air and water pollution control operations, solid waste management techniques available for a K-T indirect liquefaction facility are fewer and also more site specific. In addition, the quantities and characteristics of some solid waste streams (e.g., brines and sludges) are affected by the processes selected for air and water pollution control. Because of this, solid waste management at a K-T indirect liquefaction facility is not an isolated issue but rather an element in the total program for pollution control.

The sources and factors affecting the characteristics of the solid waste streams generated in K-T-based indirect liquefaction facilities are summarized in Table 4-45. Of the streams listed, dewatered dust from gasification operation is by far the largest volume stream. Depending on the synthesis process used, it comprises 45% to 64% of the total solid waste generated from the plant. Flue gas desulfurization (FGD) sludge from a lime/limestone process and gasifier slag are the next largest volume streams, comprising up to 35% of the total waste generated.

Coal type has considerable impact on the characteristics of the solid wastes generated, and thus the control required. Major coal properties affecting the solid waste control approaches include: ash content, sulfur content, and ash acidity/alkalinity. Coals with higher ash or sulfur contents will result in the generation of larger quantities of gasifier ash or FGD sludges, and thus will require larger control facilities.

The gasifier and boiler ash generated may be acidic or alkaline. Alkaline fly ash has been used in existing power plants to mix with FGD sludges before disposal. Mixing these two may result in a material structurally more

TABLE 4-45. SUMMARY OF SOLID WASTE STREAMS FROM K-T BASED INDIRECT LIQUEFACTION FACILITIES

Stream	Pollutants of Potential Concern	Factors Affecting Waste Stream Characteristics
From Main Process Train		
Quenched Gasifier Slag (Stream 207) Dewatered Gasifier Dust (Stream 209)	Leachable trace elements, inorganic compounds	Feed coal characteristics, gasifier operating conditions quench water characteristics.
Spent Shift Catalyst (Stream 217)	Leachable trace elements	Catalyst composition, life
Spent Sulfur Guard (Stream 218)	Leachable trace elements	Sulfur guard composition, AGR effluent gas characteristics.
Spent Methanation Catalyst (Stream 238) Spent NO_x Reduction Catalyst (Stream 212)	Leachable trace elements	Catalyst life, decommissioning procedure, synthesis gas characteristics.
Spent F-T Catalyst (Stream 222) Spent Methanol Catalyst (Stream 227) Spent Mobil M Catalyst (Stream 232)	Leachable trace elements	Catalyst life, regeneration frequency, synthesis gas characteristics
From Auxiliary Processes		
Boiler Bottom Ash (Stream 304)	Leachable trace elements	Feed coal characteristics, boiler operating conditions, slurry water characteristics.
Raw Water Treatment Sludges (Stream 300)	Leachable trace metals	Raw water characteristics, treatment system design and operation.

(continued)

TABLE 4-45. (Continued)

Stream	Pollutants of Potential Concern	Factors Affecting Waste Stream Characteristics
From Pollution Control		
Boiler Fly Ash (Stream 302)	Leachable trace elements potential dust emissions	Feed coal characteristics, boiler operating conditions, slurry water characteristics.
FGD Sludges from Boiler* (Stream 424)	Leachable trace elements	Coal sulfur content, FGD process design and operation.
Spent Claus Catalyst (Stream 402) Spent Beavon Catalyst (Stream 407) Spent SCOT Catalyst (Stream 410)	Leachable trace elements	Catalyst life, regeneration frequency, acid gas characteristics.
Fly Ash from FBC Boiler (Stream 413)	Leachable trace elements potential dust emissions	Feed coal characteristics, boiler operating conditions, sorbent carryover.
Spent Sorbent from FBC Boiler (Stream 414)	Leachable trace elements	Feed coal characteristics, FBC boiler operating conditions, sorbent characteristics.
Biological Sludge from Wastewater Treatment (Stream 415)	Leachable organics and trace metals	Wastewater treatment system design and operation.
Recovered Sulfur (Streams 403 and 408)	Vanadium and cyanides (with Beavon/Stretford only)	Coal sulfur content, bulk sulfur removal efficiency.
Collected Dust from Particulate Control (Stream 400)	Potential dust emissions	Dust collection process design and operation.

*For the wet limestone process.

suitable for landfilling. The acidity/alkalinity nature of ashes may affect their leaching characteristics and thus influence control practices.

The solid waste streams listed in Table 4-45 can be classified according to four waste type categories (source types) which are based on the nature of the waste. These waste types are: inorganic ashes, recovered by-products which prove to be unsalable, organic sludges, and spent catalysts. Several control techniques are potentially applicable to these streams.

In general, solid waste control techniques aim at containing the entire waste stream. Thus, the performance of these techniques, in terms of removal or control efficiencies, are generally 100 percent. However, unless designed and operated properly, secondary waste streams with undesirable characteristics may be generated and migrate away from the site employing the technique. For example, runoff can contaminate surface water and percolating water can contaminate ground water. The significance of this depends upon the nature of the species which might be leached out of the solids by the runoff/percolation. Thus, in selecting solid waste management techniques, the major evaluation criteria are whether the technique is applicable and economically feasible, and whether the secondary waste streams are suitablly contained.

Based upon current techniques practiced in the synfuel and other industries, together with those being considered by proposed synfuel plants, the bulk of the solid waste from K-T facilities will likely be disposed of on land. Land-based disposal techniques are by far the most site-specific techniques. The suitability of the site, as well as the design and operation of the facility would depend on the site location, transportation costs, hydrogeologic conditions, and many other factors. In short, a detailed analysis of the specific site is an important element of the overall control technique evaluation process.

Land disposal (e.g., landfill, surface impoundment, land treatment) will be subject to regulations promulgated by EPA pursuant to the Resource

Conservation and Recovery Act (RCRA), covering the generation, transport, treatment, storage, and disposal of solid wastes. Requirements concerning a solid waste can vary significantly, depending upon whether the waste is determined to be "hazardous" or "non-hazardous" as defined by RCRA regulations. In this section, no attempt is made to judge whether the various individual waste streams will be determined to be hazardous or not. Rather, treatment and disposal techniques are presented which would cover the range of possibilities, whether the waste is hazardous or non-hazardous.

Another technique potentially applicable to some solid waste streams - in addition to land disposal - is incineration. If a waste which is determined to be "hazardous" is proposed for incineration, the incinerator will have to be designed and operated in accordance with RCRA requirements.

The available techniques that may apply to the K-T solid waste streams are identified and evaluated in this section. Since no specific site is being considered, a general overview of these techniques is first presented. This is followed by an evaluation of the applicable controls to each individual stream under each waste source type. The emphasis is on identifying the applicability of the technique. For the reasons stated above and because the characteristics of many of the solid waste streams are not known, it is not possible to evaluate the optimum design and operation of these techniques in the PCTM; optimum design/operation will vary with the site. It is assumed that solid waste management facilities are captive, i.e., they only handle waste from the K-T plant.

4.3.1 Solid Waste Control

Several control techniques are potentially applicable for management of solid waste streams. These techniques are summarized in Table 4-46. As shown, they can be broadly divided into three control categories according to their functions. The three control functions are treatment, reuse/resource recovery, and disposal. Treatment may involve specific chemical/physical processes for preparing the waste to meet certain reuse/resource recovery specifications or to stabilize the waste for disposal. Reuse/recovery is one form of ultimate or final control for the waste. This approach is usually waste specific, highly dependent on market availability and cost tradeoffs, and may require specific treatment of the waste. Disposal is another form of ultimate control for the waste. Most disposal techniques are land-based techniques and thus are highly site-specific. The major site-specific factors that affect the design, operation and cost of land-based techniques are summarized in Table 4-47. The following is a brief description of the individual techniques.

TABLE 4-46. SUMMARY OF SOLID WASTE MANAGEMENT TECHNOLOGIES

Technology	Description	Operations Considerations	Reliability or Limitations	Equipment	Waste Generated	General Comments
Treatment						
Fixation/ Encapsulation	Chemicals are added to stabilize or solidify the wastes	Wide variety of wastes can be processed; the feasibility of solidifying a particular waste may differ with different process	Limited commercial experiences	May include mixing chamber, pumps, metering devices, storage tanks, chemical feed systems	Solidified waste	Most processes are applicable only to small waste streams
Incineration	Organic Wastes undergo destruction to reduce volume and toxicity	Each type of organic waste may require different operating characteristics; experienced operators required	Only organic wastes can be processed	Waste transportation machinery, incinerator	Ash; air pollution control residues	Process is energy intensive
Reuse/Resource Recovery						
Reuse, Resource Recovery	Waste is utilized in a manufacturing process, construction application, or is processed for reuse in original application, or valuable components are recovered, from waste as byproduct for marketing.	User for waste must be located; cessation of reuse requires immediate alteration of management techniques; thereby, necessitating long term contracts	Markets for wastes are limited and economic viability is heavily influenced by distance to market	Transportation vehicles	None	In general, these are the most environmentally acceptable management techniques.
Disposal						
Landfill	Site is designed, constructed, and operated to totally contain waste; features include natural or artificial liners, leachate collection and treatment systems, and groundwater monitoring system	Wide variety of wastes can be accepted; provisions must be made for incompatible wastes and reactive wastes	Waste will be contained subject to adequate site operation and maintenance and absence of extreme hydrogeological changes or earth movements	Earth moving equipment, waste handling machinery such as fork-lifts and trucks	Surface runoff and leachate	Site location and design dependent upon hydrogeological conditions; provisions must be made for site care after cessation of operations
Surface Impoundment	Site is excavated or diked to form pond to contain waste; supernatant is syphoned off and treated or allowed to evaporate	Similar to landfill	Similar to landfill	Machinery to move waste to site, usually pipelines	Supernatant and leachate	Waste may have to be removed when operation ceases; if waste remains, long term site care and maintenance program must be established
Land Treatment	Waste is treated by incorporation into the land according to specific procedures	Only limited types and mass of organic wastes can be managed	Heavily dependent upon weather conditions	Waste moving machinery, usually trucks, and waste incorporation machinery, usually bulldozers and discs	Possibly surface runoff and leachate	Site location dependent on soil conditions; provisions must be made for long term site care
Deep Well Injection	Wastes are pumped through wells into appropriate formations generally several thousand feet below the surface	Wastes frequently must be treated before injection	Injection rates frequently limited by receiving formation	Pumps, injection wells	Residues from the waste treatment process	Some states prohibit deep well injection

TABLE 4-47. SITE-SPECIFIC FACTORS TO BE CONSIDERED FOR LAND-BASED DISPOSAL OPTIONS

Climatological

- Wind conditions (e.g., speed, directional flux, dilution factors, humidity, temperature)
- Precipitation (e.g., annual precipitation, storm intensity, snow contributions)
- Evapotranspiration rate (e.g., season variations)

Geologic Factors

- Physiographic features (e.g., runoff coefficient, slope, drainage patterns, erosional features)
- Surface and subsurface geology (e.g., outcrops, bedrock features, strike and dip of the bedrock, rock composition)
- Soil types (e.g., CEC capacity, texture, permeability, stratification, homogenous vs. heterogenous deposition, chemical composition, percent of humic material)
- Seismic factors (e.g., ground shaking or rupture)

Hydrogeologic Factors

- Drainage patterns
- Stream flow (e.g., velocity, perennial vs. intermittent, effluent or influent source)
- Surface waters (e.g., tidal effects, recharge vs. discharge points)
- Vadose zone (e.g., depth, moisture content, hysteresis patterns, storage capacity)
- Groundwater (e.g., depth, number of aquifers and relationships, confined or artesian, nature of confining layer(s), capillary fringe characteristics)
- Piezometric surface (e.g., streamline flux patterns due to seasonal or event related phenomena, influence of recharge/discharge areas, streamline anomalies)
- Water quality (e.g., background vs. undersite vs. downgradient, water uses - consumptive, irrigation, recreation, point source contributors and their respective hydrogeologic pathways)
- Floodplain (100 year flood) (e.g., aerial flooding limits, degree of localized streamline pattern reversal, erosional consequences)
- Wetlands (e.g., recharge vs. discharge source, wetland/groundwater continuity and pathway)
- Recharge and discharge areas (e.g., proximity of disposal area, volume of flow)

Land Use Factors

- Historic significance
- Transportation corridor (access)
- Beneficial uses
- Cost
- Demographic setting
- Geopolitical impact
- Ultimate land use

4.3.1.1 Treatment

For the purpose of this manual, only two solid waste treatment techniques are considered. These are fixation/encapsulation, and incineration. Other techniques such as dewatering, neutralization, etc. are either considered as part of the base plant operation, or part of the pollution control processes in other media (air or water), depending on the origin of the waste.

Fixation/Encapsulation

Fixation and encapsulation are treatment processes which stabilize or solidify waste constituents, or enclose the waste within other materials. Fixation processes generally combine the concepts of solidification (the alteration of the characteristics of a waste to attain desired structural characteristics) and stabilization (the immobilization of waste constituents by chemical reactions to form insoluble compounds or by entrapment within an inert polymer or stable crystal lattice). Depending on the principal chemical agents used, fixation processes can be categorized as cement-based, lime-based, thermoplastic organic polymer-based, and glassification techniques. Encapsulation processes involve enclosing the waste in a coating or jacket of an inert, relatively impermeable material so that contact between the waste and water is prevented. Regardless of the specific chemicals used, typical fixation process operations involve mixing the chemical with the waste in a reactor at specific temperature and for a specific time period. The end product is the fixed waste. In the case of encapsulation, bulk wastes are enclosed in a stabilizing shell or container rather than being intimately mixed with a stabilizing agent.

For economic reasons, these techniques have only been applied to small volume waste streams or streams which are prone to pozzolanic reactions. Chemical requirements for fixing the latter type of streams are generally low. FGD sludge is one example of this type of stream. Several proprietary, cement- or lime-based fixation techniques have been used in fixing FGD sludges.

Typical unit costs are reported to be $10 to $17 per metric ton of sludge fixed. It is recommended that, before implementing this technique to a specific waste, detailed treatability studies with various chemical additives be performed to (1) establish that the waste is treatable, (2) select the optimal process, and (3) minimize the cost (95).

Incineration

Incineration is a controlled thermal decomposition process which reduces the weight and volume of the waste by converting many component elements of organic matter into gaseous forms. The extent of volume and weight reduction is dependent upon the waste characteristics, the incineration process, and the specific equipment used. Incineration is also a viable detoxification process if the toxicity results from the structure of the organic material as opposed to the properties of the elements it contains. The end products of incineration include carbon dioxide, water, ash, and other inorganic compounds. Incineration has been applied to various industrial wastes including refinery wastes, sewage sludge, paper mill waste liquor, pharmeceutical wastes, and organic chemical wastes. The common types of incinerators used for solid waste disposal include rotary kiln, multiple hearth, and fluid bed reactor. The annualized unit cost for a 61 GJ/hr capacity rotary kiln incinerator is estimated to be $270/Mg.

4.3.1.2 Reuse/Resource Recovery

Reuse or resource recovery of waste streams is desirable from environmental standpoint because of direct waste reduction and perhaps displacement of other resource requirements. Potential adverse environmental impacts associated with disposal of the waste are eliminated although other impacts may arise as a result of the reuse/recovery process utilized. This control approach is highly waste specific and is constrained by the availability of markets or uses for the waste.

The economics of reuse/resource recovery are sensitive to site-specific factors such as transportation costs and some general factors such as the prices of the recovered/reusable materials and the cost of preparing the waste for reuse/resource recovery. The feasibility of this control should be thoroughly analyzed for each individual facility before implementation.

4.3.1.3 Disposal

The bulk of the solid wastes from a K-T facility are likely disposed on land. Three potentially applicable techniques for these streams are discussed in this section. These are landfill, surface impoundment, and land treatment.

Landfills

Landfills have been widely used for the disposal of municipal refuse and a range of industrial wastes. In landfilling, waste is brought to the disposal site by truck or conveyor, spread in layers, and compacted with heavy equipment. In most municipal landfills the waste is covered with a thin layer of soil at the end of the working day. The process is repeated until the desired depth is reached or the available area is filled. A final cover of soil is then added. The finished site is either revegetated or prepared for other end uses.

Landfill can be accomplished in unexcavated depressions (the area-fill method) or in excavated sites (the trench-fill method). These can be natural sites or man-made sites such as coal mines. There are two major concerns in landfill design and operation. Runoff from landfill sites may contaminate surface water, and percolation from sites, after passing through the waste pile, may contaminate groundwater. Runoff/surface water contamination may be prevented by grading the site and by containment of runoff. Diversion channels should be incorporated into the initial design of the landfill and constructed before the site begins accepting waste. This prevents surface runoff water from entering the site and generating leachate.

Migration of leachate from the site can be controlled by lining the landfill with clay, concrete, asphalt, or plastic. Liners will often be required if the solid waste is considered to be hazardous and may sometimes also be desirable if the waste is nonhazardous. The choice of an appropriate liner or liners will depend on site-specific climatologic, geologic, and hydrogeologic factors, as well as on the compatability of the liner and the waste to be contained and the relative cost of compatible liners. A leachate collection and treatment system may also be necessary. Such systems consist of perforated pipes and sumps placed in a layer of permeable sand at the bottom of the fill. After being pumped out of the landfill, the collected leachate may be treated in the gasification facility's wastewater treatment system or in a separate treatment system.

In the absence of any judgment concerning whether or not a given waste might ultimately be determined to be hazardous, and in order to remain independent of site-specific factors, two landfill designs are considered in the PCTM. These two designs cover the range from the simplest set of conditions (nonhazardous waste, favorable hydrogeologic and other site conditions that preclude the need for liners) to the most complex (hazardous waste, unfavorable hydrogeologic and other site conditions which necessitate double liners). The two landfill designs are presented in Figure 4-9. For the purposes of this assessment the lined landfill design assumes an upper liner consisting of 1 m of clay and a lower liner of 0.76 mm synthetic material. Both landfill designs assume the completed fill will be 30 m above the original land surface with a slope of 3:1. Both landfills will have a final cover consisting of 0.5 m sand and 0.3 m of clay. The most complex, hazardous case would also include provisions for closure and post-closure care, monitoring, recordkeeping and other requirements.

The total capital investment and total annualized unit costs as a function of the site capacities for the two designs are presented in Figure 4-10. To be consistent with cost estimates performed for the base plant and the air and water media, no land cost is included.* The capital investment

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*About 1,100,000 m^2 of land is needed per 10^6 Mg/yr of waste generated. Assuming a land cost of $5,000/10,000 m^2 the capital investments for the lined and unlined landfills, as presented in Figure 4-10, will be increased by more than nine percent. Additional land may be required for road construction, buffer zone, buildings, etc., which will incur additional costs.

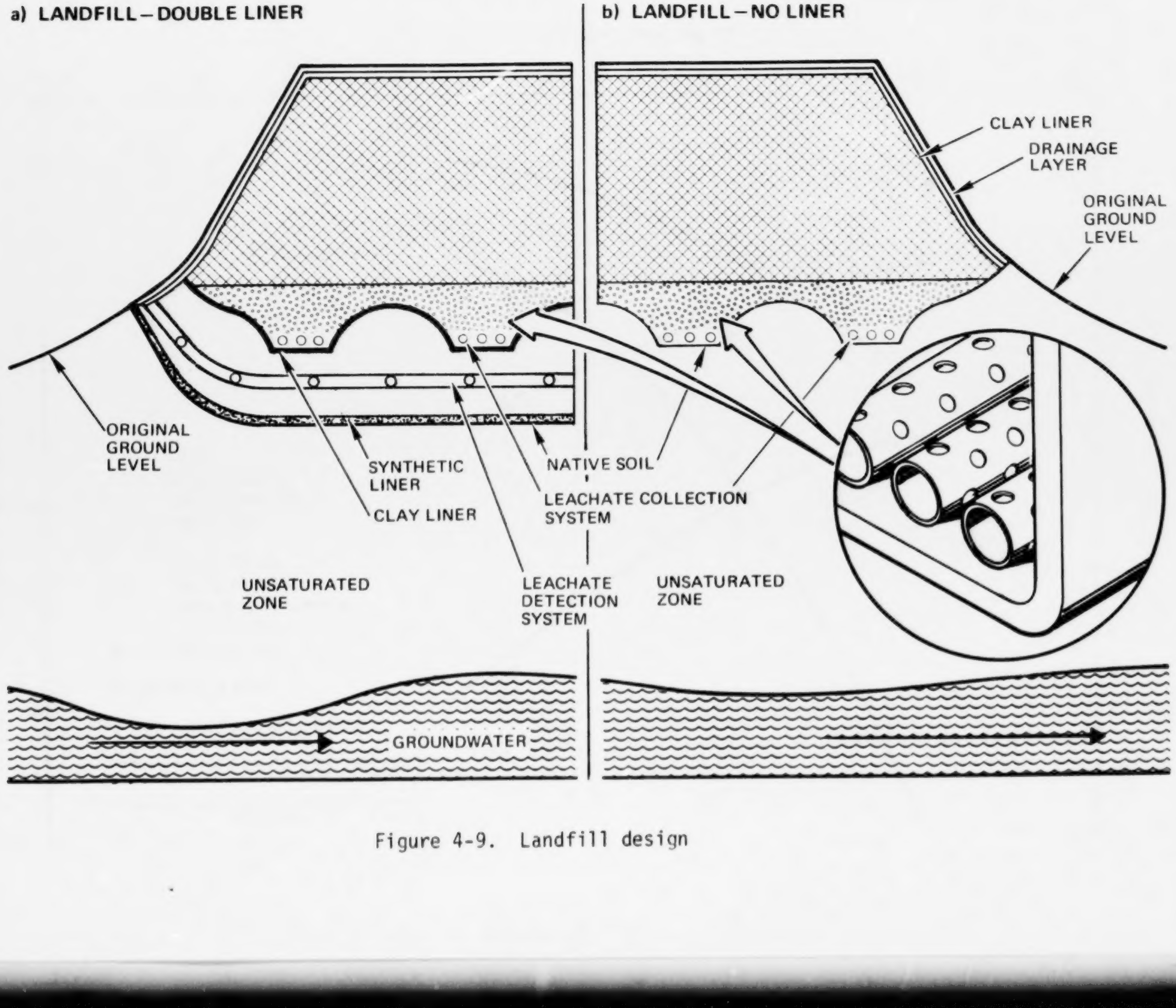
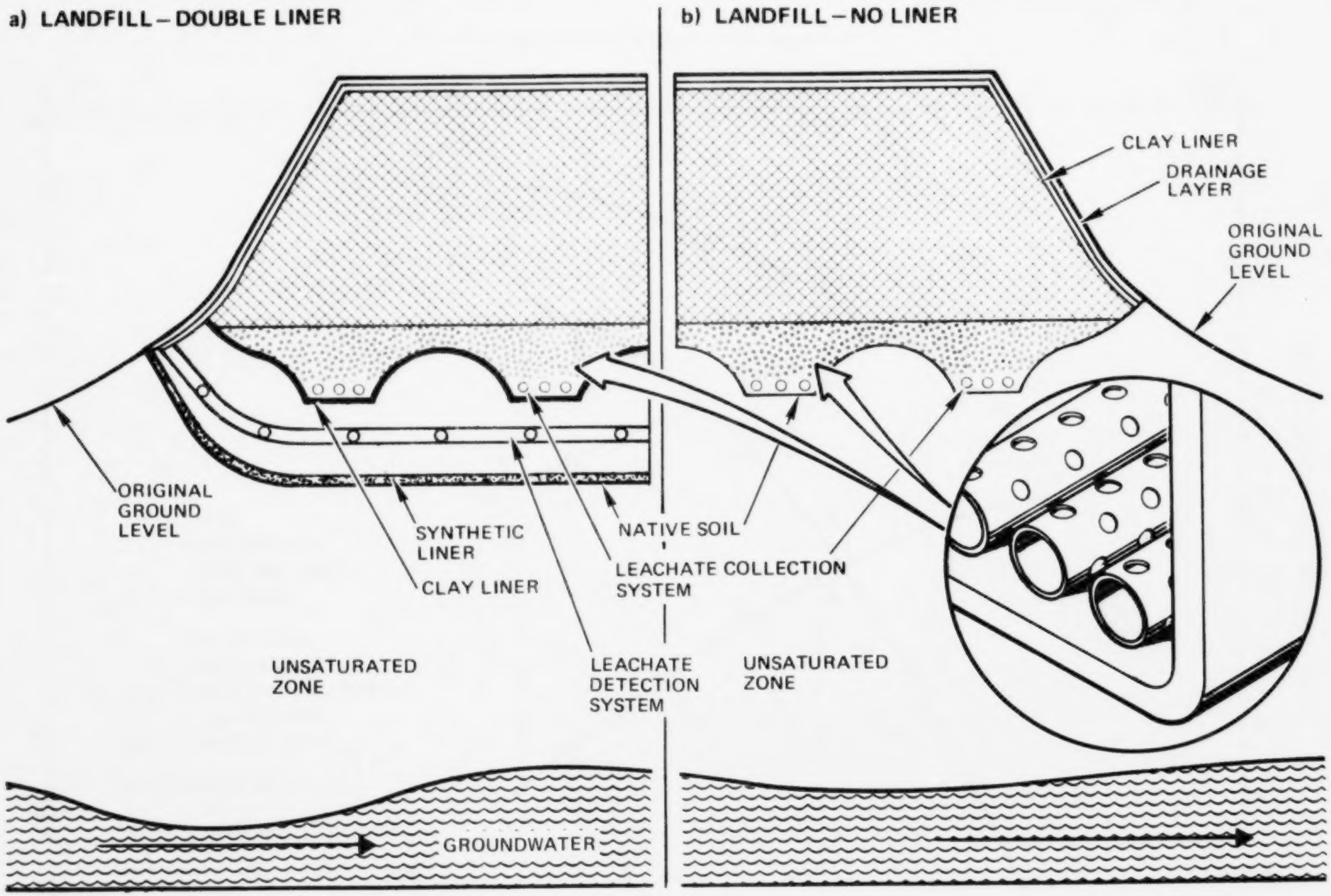


Figure 4-9. Landfill design



a) LANDFILL – DOUBLE LINER

b) LANDFILL – NO LINER

Figure 4-9. Landfill design

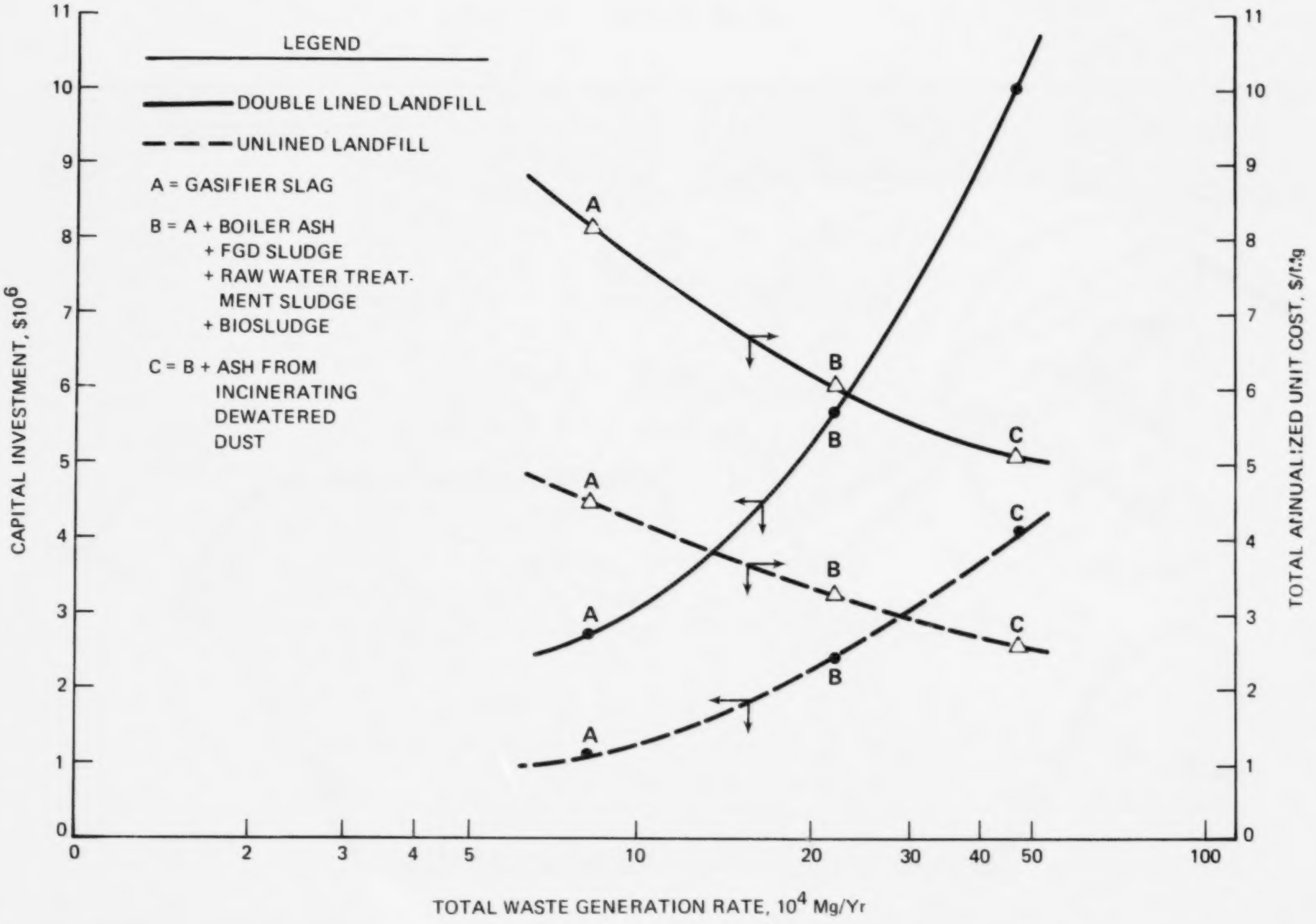


Figure 4-10. Capital investment and annualized unit cost for landfills

developed includes site preparation cost (e.g., clearing and scrubbing, groundwater monitoring and collection, liners), final cover and revegetation cost, and landfill equipment cost. It was assumed no excavation is required. The annualized cost includes labor, fuel, and amortized capital costs, but does not include hauling cost and other costs such as administrative, closure/post-closure, and liability costs. These other costs would depend on the classification of wastes under RCRA. EPA has estimated that for a 50,000 Mg/yr commercial hazardous waste landfill, administrative and other compliance costs amount to $9/Mg. Hauling cost is a function of distance between the plant and the disposal site. It is estimated that the unit cost for a round-trip distance of 5 and 15 km are $2 and $4/Mg, respectively.

Surface Impoundments

Surface impoundments have been utilized widely by municipalities and industries to process or dispose of waste liquids, sludges, and slurries. Like landfill sites, the impoundments can be in natural depressions or in excavated areas. Earthen dikes are usually constructed around the impoundment area. Wastes are transported hydraulically to the impoundment. The wastes deposit at the bottom of the impoundment, and the supernatant may be removed and treated for discharge or recycle or allowed to evaporate.

When the surface impoundment has been filled with waste, the site may be closed in one of two ways: the waste may be left in place and covered to prevent erosion and the infiltration of precipitation, or it may be removed from the impoundment site for further treatment or final disposal in a landfill. If wastes are left in place, the site becomes a landfill (subject to any requirements pertaining to a landfill), and a long-term site care and maintenance program will need to be established. The cost per unit volume for surface impoundments are expected to be similar to those of landfills with similar depths. However, since surface impoundments generally are used for the disposal of wet, not yet dewatered wastes, a larger area may be required per unit mass of dry solids, resulting in higher disposal costs (i.e. some of the disposal cost will be for "disposing" of water). Disposal cost could be reduced if the wet wastes were dewatered first, but there would be costs associated with dewatering. Similarly, disposal costs may be reduced if appreciable natural dewatering occurs within the surface impoundment due to settling and evaporation. This trade-off in cost is highly dependent upon waste characteristics and site-specific factors.

Leachate migration from surface impoundments is controlled in much the same way leachate is controlled from landfills. Diversion structures prevent runoff from surrounding terrain from entering the site; liners of in-place or compacted soils or synthetic materials retard leachate migration down into the soil and groundwater. As in the case of landfills, the PCTM considers both an unlined and a lined impoundment in order to cover the range of possible experience. The unlined impoundment represents the simplest set of conditions (nonhazardous waste with favorable site conditions). The lined impoundment represents a much more complex situation (hazardous waste with unfavorable site conditions). The two surface impoundments are presented in Figure 4-11. For the purpose of this assessment, the lined impoundment design assumes a liner consisting of 1.5 m of clay. Both designs assume the completed site will be 10 m deep. When the impoundment is filled, it is capped with a cover consisting of 0.3 m clay and 0.5 m sand to prevent infiltration of precipitation.

The capital investment for a surface impoundment with an annual capacity of 467,000 Mg/yr is estimated to be 4.3 and 12.5 million dollars, respectively, for the unlined and lined impoundment design. These costs include site preparation costs (site clearing and installation of the groundwater monitoring system and liners where required), final cover, and revegetation costs. It was assumed no excavation is required. If the whole impoundment has to be excavated, the capital investment, which includes site preparation cost, will be increased by 8 and 40 times, respectively, for the lined and non-lined

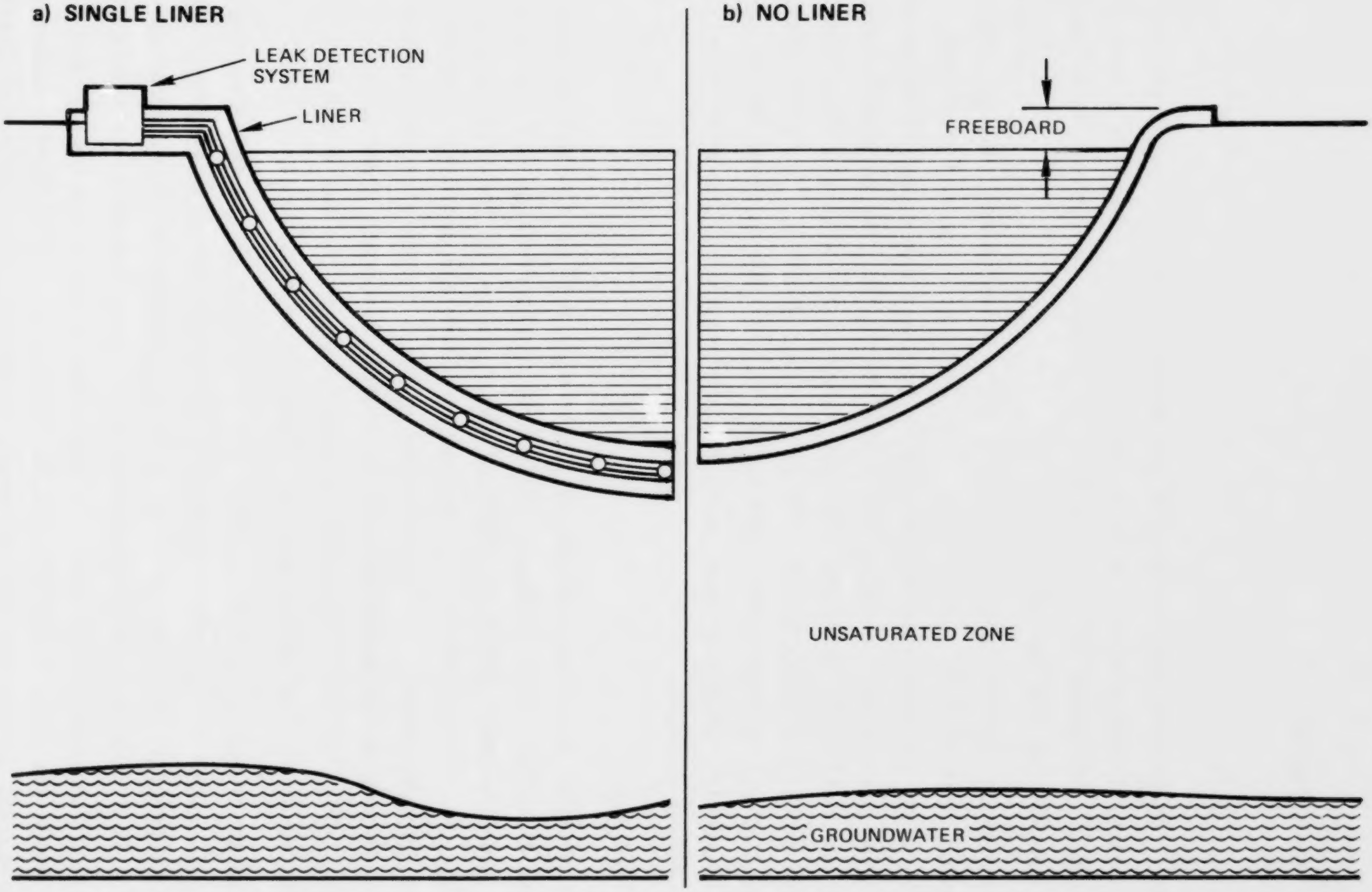


Figure 4-11. Surface impoundment design

designs. To be consistent with cost estimates for the base plant and pollution control in other media, no land cost is included. Assuming a land cost of $\$0.50/m^2$, including this cost item will increase the capital investment by 7% and 20% for the two designs.

The total annualized unit costs for the two impoundment designs are estimated to be $2.1/Mg and $5.7/Mg. This includes labor and amortized capital cost, but does not include pumping cost and other costs such as administrative, closure/post closure, and liability costs. The pumping (transportation cost) would depend on the topography of the site and the distance between the site and the plant. The other costs would depend on the classification of wastes under RCRA. EPA has estimated that for a 50,000 Mg per year commercial hazardous waste landfill, administrative and other compliance costs amount to $9/Mg.

Land Treatment

Land treatment refers to the use of land or soil as a medium to treat and dispose of waste. Also known as landfarming, landspreading, and soil application, land treatment has been practiced successfully for the treatment and disposal of municipal wastewater treatment sludges and petroleum industry oily wastes for many years. It relies on the ability of naturally occurring soil microorganisms to decompose and utilize organic compounds under aerobic conditions. The design and operation of land treatment systems would be affected by whether or not the wastes were considered to be hazardous.

Wastes added to soil are subject to one or more of the following processes: (1) decomposition/degradation; (2) leaching; (3) volatilization; and (4) incorporation into the soil matrix (e.g., through ion-exchange or adsorption). It is the degradation processes which treat the waste to reduce its objectionable properties; these processes must be maximized during land treatment, while the other processes must be minimized or eliminated. Applying biodegradable wastes, maintaining proper (aerobic) conditions for microbial action, and avoiding or pretreating wastes which are toxic to the microorganisms will encourage degradation processes. Proper site selection and proper site management will minimize leaching and subsequent contamination of groundwater. If volatile wastes are to be land-treated, subsurface injection of the wastes or immediate tilling after application will minimize air pollution.

Wastes with high concentrations of toxic substances such as arsenic, cadmium, lead, and mercury should not be land treated in sites where food chain crops are grown, as they may be incorporated into the soil and taken up by plants. Prior to land treating the biological oxidation sludge, long term studies should be performed to confirm that the waste is degradable in the soil, that there is no accumulation of non-degradable toxic substances in the soil, and to establish the area required for the particular soil-waste combination at hand.

Assuming biosludge is applied 10 times/yr, with an application rate of 0.015 Mg/m^2/application and a factor of 2 to account for land required for roads, buffer zones, dikes, etc., it is estimated that 280,000 m^2 of land is required to land treat 21,000 Mg/yr of biosludge. The annualized unit cost for this is estimated to be $7.6/Mg.

4.3.2 Inorganic Ashes and Sludges

Table 4-48 summarizes the flow rates of the waste streams that consist primarily of inorganic ashes or sludges. These streams are the largest volume solid waste streams from a K-T based indirect liquefaction plant. The application of the available control techniques to these specific waste streams from K-T plants are evaluated in this section.

TABLE 4-48. ESTIMATED FLOW RATES FOR THE INORGANIC ASH AND SLUDGE STREAMS

Stream Description	Stream Flow, Kg/hr
Gasifier Slag (Stream 207)	10,371
Dewatered Gasifier Dust (Stream 209)	59,217
Boiler Bottom Ash (Stream 304)	745
Boiler Fly Ash (Stream 302)	2,980
FGD Sludge (Stream 424)	10,722
Raw Water Treatment Sludge (Stream 300)	432

4.3.2.1 Gasifier Slag (Stream 207)

The gasifier slag is a coarse pebble-sized material which is physically stable and essentially chemically inert. As discussed in Section 3, this stream is essentially coal ash with little or no carbon if the gasifier is operated properly. Leachate may include low levels of trace elements (see Table 3-7 for laboratory leachate characteristics). Tests of leachate for organics have not been conducted, but organic levels would be expected to be low. Potential may exist for very low level H_2S evolution from the slag, particularly under acidic conditions, as a result of sulfide present in the interstitial water or due to the reaction of metallic sulfides in the slag. However, due to the low sulfur content of the slag and interstitial water, the potential for sulfide evolution appears to be low. The following techniques are applicable to controlling this stream.

Treatment

The techniques applicable to treatment of gasifier ash are fixation and encapsulation. Treatment of gasifier slag may be appropriate if future data indicate that significant concentrations of trace metals are in leachate from the gasifier ash. Currently available leach data indicate the trace elements in the leachate are low and should not be significantly different from conventional coal boiler bottom ash.

The performance of treating this stream is dependent upon the specific process (additive agent) used, and can only be established after thorough treatability studies. The cost for treating this stream is also dependent upon the process used. Assuming that the fixation processes which have been applied to FGD sludge are applicable to treating this stream, the unit cost will be about $10 to $17 per Mg (95-98).

Resource Recovery

Gasifier slag may be utilized in a number of commercial applications, just as boiler bottom and fly ash from fossil-fueled power plants have been used. The National Ash Association reported that 24.3 percent of the coal boiler ash produced in 1977 was reused in commercial applications. Ash has been used commercially as a partial replacement for cement in concrete, as fill material for roads and other construction projects, and as blast grit and roofing granules. The slag may need to be crushed and sized before it can be used in such applications.

The major constraints on reuse of gasifier ash are those of the market for the material. Market conditions will vary from site to site. Given the fact that not all ashes from existing power plants are commercially utilized, it may be difficult to find markets where all or significant quantities of the slag from the K-T facility can be reused. Users for the slag will likely be limited to those who are located in the vicinity of the plant. The economic viability of reuse decreases with increasing distance to market and hence increasing transportation costs. If market conditions change so that commercial reuse ceases, the waste management techniques for the ash will need to be altered. Long-term contracts with users may lessen the potential for market interruptions.

Disposal

Gasifier slag can be disposed of in two ways: in landfills or in impoundments.

Landfill --

In landfilling, gasifier slags are usually brought to the site by trucks, spread on the surface of land or previously placed ashes, and compacted. As the pile height increases, a working face with safety slope (assumed to be 3:1) is developed to ensure stability of the fill.

If the gasifier slag is determined to be nonhazardous, then in the most favorable case (e.g., favorable site conditions), an unlined landfill might be possible. On the other hand, if the wastes were considered to contain hazardous components, a lined landfill would be necessary where hydrogeologic or other site factors are unfavorable.

Based on current and proposed practices in the synfuel and other industries, this stream is likely to be co-disposed with some other solid waste streams from the plant in one common landfill. Although more than one landfill/disposal facility (e.g., one landfill design for hazardous waste and one landfill for nonhazardous waste) may be operated in a K-T facility, for costing purposes in the PCTM, one landfill accepting the wastes from the K-T plant is assumed. By considering the alternatives of all wastes being disposed of in a nonhazardous waste landfill with no liner and in a hazardous waste landfill with double liners, the range of landfill cost estimates in the PCTM should bracket the costs that might be encountered in practice for any split of the wastes between hazardous and nonhazardous categories.

Assuming a landfill is designed to accept the gasifier slag, boiler bottom and fly ash, FGD sludge, and raw water treatment sludges, the capacity of the landfill would be 200,000 Mg/yr. As shown in Figure 4-10, the annualized unit cost for the unlined and lined landfill design will be $3.2/Mg and $5.9/Mg, respectively. The total annualized cost that would be attributable to the gasifier slag stream alone would be $262,000/yr and $482,000/yr, respectively, for the two landfill designs.

If the gasifier slag were disposed by itself in a separate, dedicated landfill, annualized unit costs for this smaller landfill ($82,000 Mg/yr) would be $4.5/Mg and $8.2/Mg for a nonlined and lined landfill, respecitvely. The total annualized cost for this case would be $370,000/yr and $670,000/yr, respectively.

Surface Impoundment --

One major difference between disposing the slag in a landfill and surface impoundment is the means of transporting the slag to the disposal site. Surface impoundment is usually used for storage or disposal of wet ashes which are transported hydraulically to the impoundment in a fluid state. For storage impoundments, the ashes are dredged periodically and disposed of in landfills. For disposal impoundments, the ashes are left in place and are covered to prevent erosion and infiltration of precipitation. The unit cost for surface impoundment would be similar to the cost of landfill, assuming no excavation is required. The total disposal cost may be higher because surface impoundments generally are used for the disposal of wet, not yet dewatered wastes; extra capacity is needed for the water content in the waste.

4.3.2.2 Dewatered Gasifier Dust (Stream 209)

The gasifier dust is the largest volume solid waste stream from a K-T methanol plant using Illinois No. 6 coal as feed. As presented in Section 3.3.1, this stream is estimated to be generated at a rate of 59.2 Mg/hr, and is assumed to contain approximately 50% water, 30% ash, and 20% carbon.

The dust has a high affinity for water and is likely to have poor structural stability at moisture contents exceeding 60% (99).

Treatment

Treatment with cement-based or other fixation techniques may be practiced to improve the stability of the dust when deposited on land. Several proprietary fixation techniques are commercially available. However the performance of these processes when applied to this stream cannot be assessed without thorough treatability studies. One potential problem in fixing this stream is that it may be difficult to engage the dust in pozzolanic reactions with the chemical additives. Although in principle the ash content of the stream is capable of engaging in pozzolanic reactions with the chemical agents added, the ash may not be available due to the coating effect of the carbon. The net effect may be that much more chemical agent is needed, and considering the size of the waste stream, associated costs may be prohibitive.

Resource Recovery

Due to its high carbon content, the dewatered gasifier dust can be used as fuel in a boiler. However, this material presents two major problems with respect to conventional pulverized coal-fired boilers. First, extensive drying, and thus special handling and drying equipment, is needed due to its high water content. Second, the dust contains little or no volatiles and may result in flame stability problems unless a readily combustible supplemental fuel is added or other countermeasures are taken. For these reasons, the use of fluidized bed combustion (FBC) boiler is being considered for the North Alabama Coal Gasification Consortium Project; this approach is used as an example in this section to illustrate a resource recovery alternative.

An FBC boiler is comprised of a granular bed material which is suspended or "fluidized" by a stream of air. The fuel is injected into this bed and burned. Alkaline sorbents, typically limestone or dolomite, are also injected into the bed to react with SO_2 formed during the combustion of high sulfur fuels. The inert material of the fuel in part exits the top part of the bed with the flue gas, and remainder is removed from the bottom of the bed with the spent sorbent.

The secondary waste streams generated from the FBC boiler include a flue gas stream and a spent sorbent stream. The estimated characteristics of these two streams are presented in Table 4-49. The applicable control techniques for the spent sorbent stream are discussed in Section 4.3.2.6 and the flue gas control techniques are discussed in Section 4.1. Because of subsequent particulate emission controls applied, essentially all of the ash in the flue gas will be captured and will appear as a solid waste stream. The control for this fly ash stream is discussed in Section 4.3.2.7.

The feasibility of burning the gasifier dust is highly dependent upon the cost of displaced fuel (i.e., coal), cost and availability of land. and other site-specific factors. Table 4-50 presents the estimated costs for such an application assuming zero credit for the steam generated. The capital investment presented is factored from cost estimates developed for coal-fired FBC boilers. As shown, burning the gasifier dust in the FBC boiler would cost \$8.4/Mg. However, it is estimated that about 6.3×10^5 Mg/yr of steam will be generated and if a steam credit of \$6.2/Mg were assumed, the FBC boiler cost would break even, i.e., the steam credit would offset the capitalized and operating cost. As discussed previously, a K-T facility is expected to be self-sufficient with respect to steam and, as such, steam from an FBC boiler would probably be used to generate electric power. However, the appropriate credit for power generated by dust combustion in a self-sufficient K-T facility cannot be assessed without a detailed energy balance around the plant and more detailed cost estimates for the boilers. Performing such analyses is outside the scope of this manual and, hence, no credit has been taken for generated power.

TABLE 4-49. CHARACTERISTICS OF FLUE GAS AND SPENT BED MEDIA FROM FBC BOILER

Component	Flue Gas (Stream 413)* Kmol/hr	Flue Gas (Stream 413)* Kg/hr	Spent Bed Media (Stream 414)† Kg/hr
CO_2	892	39,278	
N_2	4,415	123,664	
H_2O	1,773	31,916	
SO_2	13	838	
O_2	273	8,746	
Ar	53	2,109	
Fly Ash		1,846	
Total	7,419	208,397	
$CaSO_4$			1,603
CaO			1,221
$CaCO_3$			177
Inert			393
Total			3,394

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[*] NO_x is approximately 150 ng/J which is equivalent to 56 kg/hr (as NO_2).

[†] Characteristics of spent bed media are calculated based upon the model presented on page 366 of Reference 87.

TABLE 4-50. ESTIMATED CAPITAL INVESTMENT AND TOTAL ANNUALIZED COST FOR BURNING DEWATERED GASIFIER DUST IN FBC BOILER

Item	FBC Boiler
Capital Investment, $\$10^6$	15.6
Total Annualized Cost, $\$10^6$	3.9
Total Annualized Unit Cost, \$/Mg	8.4
% Base Plant Capital Investment	1.4
% Base Plant Total Annualized Cost	1.1

One other factor that affects the economics of this alternative is the total amount of solid waste being generated. Burning the dust will reduce the quantity of final waste by more than 60% (from 59.2 Mg/hr of dewatered gasifier dust to 21.7 Mg/hr of dry FBC boiler ash and spent bed media). In addition, power generated by FBC for in-plant use will result in less coal being fed to the pulverized-coal-fired boiler (in self-sufficient facilities); thus, less ash and FGD sludge will be generated from that part of the plant. It is estimated that about 8.9 Mg/hr of coal would be displaced by the burning of the gasifier dust. This amounts to a reduction of the coal-fired boiler size and the associated ash and FGD sludge generated by 35% (see Table 3-30). As presented in Table 4-48, a 35% reduction in boiler ash and FGD sludges amounts to about 5 Mg/hr. Thus, in effect, the use of FBC boiler for burning dewatered gasifier dust will reduce the total solid waste that is sent to ultimate disposal by 32.5 Mg/hr.

Assuming the ash from the FBC boiler is co-disposed with other inorganic streams (gasifier slag, boiler bottom and fly ash, FGD sludge, and raw water treatment sludge), the landfill capacity would be 37,000 Mg/yr. The unit annualized cost for this size landfill would be \$2.7/Mg and \$5.4/Mg, depending on whether the landfill is lined or not (see Figure 4-10). Assuming these unit costs apply, a reduction of 32.5 Mg/hr of waste quantity would amount to savings of 0.7 and 1.4 million dollars per year, respectively. The incremental total annualized cost for disposing of the FBC boiler ash and spent bed media (21.7 Mg/hr) would be $460,000/yr and $920,000/yr, respectively.

Disposal

The applicable disposal technique for controlling gasification dust is surface impoundment. Landfill can also be used if the structural stability of the dust is improved by fixation techniques. When disposing of the gasifier dust in a surface impoundment, no mechanical dewatering pretreatment is required. Quenched gasifier dust is transported to the site hydraulically. The dust settles to the bottom of the site. Excess water is recycled and reused as quench water. When the site is filled, it is capped with a cover consisting of 0.3 m clay and 0.5 m sand to avoid infiltration. It is assumed that the water content of the dust at the finished site is 50%. Mechanical dewatering of the dust prior to impoundment can reduce the pond area needed and may be employed where land is costly or of limited availability.

As discussed in Section 4.3.1.3, two surface impoundment designs are considered in the PCTM to cover the range of possible experience. Table 4-51 summarizes the estimated costs for the two surface impoundment designs as shown in Figure 4-11. The total capital investment for the non-lined and lined designs are, respectively, 4.3 and 12.5 million dollars, and the total annualized unit costs are $2.10 and $5.70/Mg.

TABLE 4-51. SUMMARY OF CAPITAL INVESTMENT AND TOTAL ANNUALIZED COST FOR DISPOSING OF GASIFIER DUST IN SURFACE IMPOUNDMENT

Item	Lined Surface Impoundment	Non-Lined Surface Impoundment
Capital Investment, 10^6\$	12.5	4.3
Total Annualized Cost, 10^6\$	2.5	0.9
Total Annualized Unit Cost, \$/Mg	2.1	5.7
% Base Plant Capital Investment	1.1	0.4
% Base Plant Annualized Cost	0.7	0.3

4.3.2.3 Boiler Bottom Ash (Stream 304)

The applicable control techniques for boiler bottom ash are similar to those for the gasification slag. Where landfill is the technique selected, the stream is likely co-disposed with other solid waste streams in one common landfill.

As discussed in Section 4.3.2.1, annualized unit costs for landfilling the solid waste streams in a common landfill are estimated to be \$3.2/Mg and \$5.9/Mg, respectively, for a non-lined and lined landfill. Based on these unit costs, the incremental annualized disposal cost attributable to this stream would be \$18,000/yr and \$34,000/yr, respectively.

4.3.2.4 Boiler Fly Ash (Stream 302)

Applicable control techniques for this stream are similar to those discussed for the gasification slag. Available technology requires that gasifier slag and boiler bottom ash be quenched before any subsequent handling of disposal. Boiler fly ash, however, may be collected and handled dry (via a dry ESP or baghouse) or wet (via a wet ESP or scrubber). The choice of collection technology depends in part on site-specific disposal factors and also on factors specific to coal type. Some fly ashes tend to undergo fixation reactions when wetted, much as Portland cement does. Recently, more power plants are converting to dry collection systems for boiler fly ash. When boiler fly ash is collected and handled entirely in the dry form, it can be potentially recovered as a resource.

Where landfill is the disposal technique selected, this stream is likely co-disposed with other solid waste streams in one common landfill. As discussed in Section 4.3.2.1, annualized unit costs for landfilling the solid waste streams in a common landfill are estimated to be \$3.2/Mr and \$5.9/Mg, respectively, for a non-lined and lined landfill. Based on these unit costs, the incremental disposal cost attributable to this stream would be \$74,000/yr and \$136,000/yr, respectively.

4.3.2.5 Boiler FGD Sludge (Stream 424)

Applicable techniques for controlling FGD sludge include fixation, surface impoundment and landfills. These techniques have been widely used in disposing of FGD sludges from existing coal-fired power plants.

Treatment - Fixation

FGD sludge typically contains 30 to 50 percent solids after thickening or filtration. It is a poor landfill material in this form because it is thixotropic. To rectify this problem, treatment by fixation may be practiced. Several patented processes are available commercially for fixing FGD sludges. One mixes the sludge with boiler fly ash and lime while another adds a proprietary chemical (basically a cementitious agent) as the hardening material. Typically these proprietary processes involve dewatering the sludge and combining the sludge with proprietary additives which promote pozzolanic reactions, resulting in a material less leachable, less permeable, and structurally more suitable for landfill. Proprietary methods which have been successfully applied to fixing FGD sludges include Chemfix (addition of Portland cement and sodium silicate), Calcilox (calcined blast furnace slag and lime), IUCS - Poz - O - Tec (fly ash and lime under controlled temperature and moisture conditions), ICT (lime, betonite, and cement), and Research-Cottrell (sludge dewatering prior to fly ash admixing).

Unit cost for these treatments ranges from $10 to $17 per Mg of sludge fixed. Another treatment alternative practiced in many coal-fired power plants is mixing the FGD sludge with boiler bottom and fly ash before disposal. For coals that generate ashes that are alkaline, mixing the ash with the sludge will also initiate pozzolanic reactions.

Disposal

Disposal techniques applicable to FGD sludge include landfill and surface impoundment. Because of its low solids content and structural instability, FGD sludge may be treated by fixation or mixing with boiler fly ash prior to disposal. The use of surface impoundments will reduce the liquid content of the sludge, but the dried solids are readily soluble when exposed to moisture after disposal, so proper surface impoundment closure is essential.

Assuming this stream is mixed with the gasifier slag, boiler bottom ash and fly ash, and raw water treatment sludge before disposal in a common landfill, the unit disposal cost for a non-lined and a lined landfill is estimated to be \$3.2/Mg and \$5.9/Mg, respectively (see Section 4.3.2.1). The incremental annualized cost attributable to this stream would be \$270,000/yr and \$500,000/yr, respectively.

4.3.2.6 Spent Sorbent from FBC Boiler (Stream 414)

The characteristics of this material are similar to the solids in the FGD sludge stream. Thus the applicable control techniques are similar to those for the FGD sludge with the exception that since this is a dry material, it can be landfilled directly without fixation. When landfill is the technique selected this stream is likely combined with other solid waste streams and disposed of in one common landfill.

4.3.2.7 Fly Ash from FBC Boiler (Stream 413)

The applicable control techniques for this stream are identical to those for Boiler Fly Ash.

4.3.2.8 Raw Water Treatment Sludge (Stream 300)

The applicable treatment and disposal techniques for this stream would be similar to those for the FGD sludge, except that the optimum fixation process and hence the treatment cost may differ. Where landfill is the technique selected, this stream is likely co-disposed with other solid waste streams in one common landfill. Assuming unit costs of $3.2/Mg and $5.9/Mg respectively, for a non-lined and lined landfill, disposing this stream will cost $11,000 and $20,000/yr.

4.3.3 Recovered By-Products

This source type includes elemental sulfur recovered from the bulk sulfur removal processes and collected dust from particulate control, if either of these materials proves to be unsalable. The flow rate of these two streams is estimated to be, respectively, 8.3 Mg/hr and 0.14 to 1.9 Mg/hr.

4.3.3.1 Recovered Elemental Sulfur (Streams 403 and 408)

Recovered elemental sulfur can be sold as by-product. However, the sulfur may be contaminated with carbonaceous impurities (from Claus plant) or vanadates, thiosulfates and thiocyanate salts (from Beavon Stretford tailgas treatment unit), making it non-marketable without further in-plant processing. If the sulfur cannot be sold, it may be disposed of in landfills.

There is a potential for elemental sulfur to be oxidized in a landfill environment, and such oxidation results in acid generation. Acidic leachate could solublize trace elements from other wastes in the landfill. Hence, it may be desirable to co-dispose waste elemental sulfur with alkaline wastes such as FGD sludges or spent FBC sorbent.

4.3.3.2 Collected Coal Dust from Particulate Control (Stream 400)

This secondary waste stream consists primarily of coal dust collected throughout the coal preparation operations. This dust can be reused as feed to the gasifier or boiler, or can be disposed of in landfills. When landfilled, spraying the dust with water may be required to reduce dust emission.

4.3.4 Organic Sludges

This waste category includes one stream, namely, the biosludge from the biological treatment process (Stream 415). This is a secondary waste stream; the flow rate of this stream has been estimated to be 2.65 Mg/hr, assuming water is used in the cyanide wash operation in the base plant. Impact of cyanide wash design on the wastewater characteristics, and thus the biosludge characteristics have been presented in Sections 3.4 and 4.2.

Treatment

Although no data are available on the composition of this waste at present, it is highly probable that some of the nonbiodegradable toxic organics that might have been present in the raw process liquor (such as polycyclic organics and aromatic amines) will end up in the sludge through sorption. These organics can be destroyed by incineration.

Incineration -- Incineration of municipal and industrial biological oxidation sludges has been practiced for many years. The application of this treatment technique to this organic sludge could be expected to destroy greater than 99% of most organics and reduce the quantity of waste that requires ultimate disposal. Assuming the biosludge is 20% solids and 70% of the solids are volatile, the total waste quantity will be reduced by 94% through incineration.

Table 4-52 presents the estimated costs for incinerating the biosludge in a rotary kiln incinerator (63 GJ/hr energy input) with energy recovery. The heating value of the biosludge was assumed to be 23 MJ/kg. As shown in Table 4-52, the capital investment for incineration is estimated to be 14 to 16 million dollars; the total annualized cost is 5.8 million dollars per year, or about $270/MG.

TABLE 4-52. ESTIMATED TREATMENT/DISPOSAL COST FOR BIOSLUDGE

Item	Incineration	Land Treatment
Total Capital Investment, $\$10^6$	14 to 16	0.5
Total Annualized Cost, $\$10^6$	5.8	0.2
Annualized Unit Cost, $/Mg	270	7.60
% Base Plant Capital Investment	1.2 to 1.4	0.05
% Base Plant Annualized Cost	1.6	0.06

Two secondary waste streams are generated by this process, namely, a flue gas stream and a residue stream. It is not possible to estimate the characteristics of the flue gas, but the cost for controlling this is included in the incinerator cost estimates presented in Table 4-52. The incinerator is assumed to be equipped with a scrubber for particulate control.

The flow rate of the residue stream is estimated to be 0.16 Mg/hr. Assuming a 99.9% destruction of organics, the residue is expected to contain about 0.33% organics and other inert materials. Most of the trace metals originally present in the biosludge will accumulate in the residue. Applicable treatment/disposal techniques include fixation/encapsulation and landfill.

Disposal

Biological treatment sludges may be disposed of in landfills, surface impoundment or by land treatment. Landfill and surface impoundment have been discussed in the previous sections. The following is a brief description of land treatment of biosludge.

Land Treatment --

In land treatment, biological treatment sludge may or may not require dewatering prior to applying to the land. Depending on the physical state, or the degree of dewatering performed, the sludges are transported to the land treatment site either by truck or hydraulic means. The sludges on land are spread with bulldozers, loaders, graders, or box spreaders. The site is generally subdivided into several plots which are treated in sequence. After waste application and evaporation of any associated water, the plot is plowed periodically until the waste has been decomposed. Chemicals such as nitrogen, phosphorus, and potassium may be added periodically as nutrients, and neutralizing agents (e.g., lime) may be added to maintain the proper pH level (7 to 9).

The estimated costs for land treating the biosludges are summarized in Table 4-52. The capital investment presented in Table 4-52 includes land preparation costs ($0.52/m^2), waste spreading equipment costs ($160,000), and monitoring well costs ($25,000). The annualized costs include labor cost, fuel cost, monitoring cost, maintenance cost, and amortized capital costs. No land nor transportation cost was included in the cost presented. It is estimated that about 32,000 m^2 of land is required. Assuming a unit land cost of $0.50/m^2, this would increase the total capital investment by more than 25%. Depending on the distance, including the transportation cost may more than double the annualized unit costs presented.

4.3.5 Spent Catalyst and Sulfur Guard

Nine types of catalysts may potentially be used in a K-T based indirect liquefaction plant. These materials eventually become deactivated and require decommissioning and disposal. Spent sulfur guard, which is not a catalyst, is also included in this discussion because (1) this is also a small volume, intermittant stream, and (2) applicable controls are similar. Table 4-53 summarizes the estimated spent catalyst generation rates. It should be pointed out that although the flow rates are presented in Mg/yr, these streams only occur intermittantly, about once every three to five years.

TABLE 4-53. ESTIMATED GENERATION RATES FOR SPENT CATALYSTS AND SULFUR GUARD

Catalyst/Guard Material	Generation Rate, Mg/yr
Spent Shift Catalyst (Stream 217)	14 - 24
Spent Sulfur Guard (Stream 218)	80
Methanol Synthesis Catalyst (Stream 227)	60 -100
Spent Methanation Catalyst (Stream 238)	40
Spent Claus Catalyst (Stream 402)	10
Spent SCOT Catalyst (Stream 410)	3
Spent Beavon Catalyst (Stream 407)	5
Spent Mobil Synthesis Catalyst (Stream 232)	300
Spent F-T Synthesis Catalyst (Stream 222)	3500
Spent NO_x Reduction Catalyst (Stream 212)	16 - 27

Due to the proprietary nature of most catalysts, there is little information available on the reuse and disposal techniques applicable to specific catalysts. Because of this, spent catalyst reuse, treatment, and disposal are discussed in general terms in the following sections, with only brief mention of specific techniques and their applicability to individual catalysts.

Treatment

Spent catalysts may be chemically fixed or encapsulated before final disposal to prevent leaching of undesirable substances. When fixing these with cement-based techniques, the weight of the fixed material may be twice its original weight; i.e., a 1:1 chemical/spent catalyst ratio may be needed. As discussed before, the performance and cost for this alternative can only be established after thorough treatability studies.

Resource Recovery and Reuse

Spent catalysts may be reused after reactivation by a contractor or the original vendor. Also, the metal components of the catalyst may be recovered for other uses. The economics of the required regeneration processes and the market value of the metals will determine whether recovery and reuse are possible. In practice, return of the spent catalyst to the vendor for processing will likely be the approach of choice in many cases.

Because of the current tight cobalt supply and the high demand for this metal, it appears that the cobalt-based shift catalyst could be economically recovered. Increasing cobalt prices have fostered interest by catalyst manufacturers to develop improved methods to regenerate the catalyst, to recover the metal, and to search for other catalysts (mainly nickel-based) which can be used in place of the cobalt-based shift catalyst.

Regeneration of spent sulfur guard, Claus catalyst, Mobil M synthesis catalyst, and Fischer-Tropsch synthesis catalyst is expected to be economically unattractive because of the low market values of the base materials of these catalysts (zinc for sulfur guard, bauxite for Claus catalyst, zeolite for Mobil M synthesis catalyst, and iron for Fischer-Tropsch synthesis catalyst). Spent methanation catalyst (nickel-based) and Fischer-Tropsch synthesis catalyst (iron oxide-based), although deactivated as far as catalyst activity is concerned, still have a large capacity for adsorption of sulfur compounds and can be used as sulfur guard bed material.

Disposal

Spent catalysts and sulfur guards may be chemically fixed or encapsulated before final disposal to minimize leaching of toxic substances or they may be disposed of once they are decommissioned. When disposed of, these materials are likely to be placed in landfills (i.e., assuming that these wastes are disposed of in a common landfill along with other plant solid waste). As indicated in Table 4-53, the overall spent catalyst generation rate is largely dependent upon the synthesis process incorporated in the plant. As discussed before, the unit costs would be \$3.2/Mg and \$5.9/Mg, respectively, for a non-lined and lined landfill; the incremental annual disposal cost for these materials would range from \$720 to \$22,000, depending on the landfill design and the synthesis process used.

SECTION 5

DATA GAPS AND LIMITATIONS

Because of the inherent gaps and limitations which exist in the data base used to support this document, it is important for readers to understand the extent to which the performance and cost estimates presented here are supported by actual operating data, extrapolations from closely related applications, or engineering calculations and/or judgements. The purpose of this section, therefore, is to convey to the reader a sense of the applicability and completeness of the data base. This information should contribute to a better understanding of how this document should be used by indicating the confidence which can be placed in the uncontrolled discharge rates and the effectiveness of specific controls.

Since the early 1970s the EPA has sponsored a significant environmental assessment program addressing synthetic fuels from coal technologies. This work has involved a combination of theoretical studies and plant data acquisition programs. These efforts have contributed both data and background knowledge used in the development of this manual. The major data acquisition programs sponsored or cosponsored by the EPA which have provided background data used in the development of this PCTM are listed in Table 5-1, at the end of this section. As indicated, the data encompass specific research projects, pilot-level sampling and analysis projects, and source sampling of foreign and domestic commercial production facilities.

Waste streams which are unique to K-T based indirect liquefaction facilities have been emphasized in this section. These streams differ from waste streams generated in other industries because of their composition and/or the approaches applicable to their control. Waste streams which do not differ in composition from wastes generated in other industries and which do not require special consideration with respect to control approaches (e.g., boiler flue gas, coal pile runoff, raw water treatment sludges, and boiler ash) are not considered in this section. These non-unique waste streams have not been considered because any significant data limitations or gaps related to their characterization have been a concern in other industries, and programs to fill identified data gaps are already underway or are currently being planned. Key data sources and the bases for characterization estimates, data gaps and limitations, and research needs relating to unique waste streams are summarized by waste medium in Tables 5-2 through 5-4 at the end of this section. Similar information relating to applicable pollution control technologies and associated secondary waste streams are presented in these tables following each waste stream or group of waste streams combined for common treatment.

In general, estimates of characteristics of the uncontrolled unique waste streams were based upon data from commercial scale K-T gasification facilities (e.g., AECI Limited, Modderfontein, South Africa and the Nitrogeneous Ferterlizer Inudstry, S.A., Ptolemais, Greece). Although these facilities produce hydrogen for ammonia manufacture, many of the individual process operations upstream of product synthesis are similar to those proposed for indirect liquefaction facilities. Data from these operations have in some instances been used directly or have been extrapolated, consistent with proposed designs. Waste characterization data for F-T, methanol, and Mobil M-gasoline synthesis processes have been based upon published designs for commercial scale facilities.

Since none of the existing K-T gasification facilities employ the range of pollution controls which are likely to be utilized in the U.S., little direct operating experience is available to accurately predict the performance or costs of applicable controls. For certain control systems (e.g., Claus bulk sulfur recovery and Wellman-Lord tail gas treatment) the existing data base from related applications is sufficient to indicate gross pollutant removal efficiencies and associated costs reasonably well. However, for control systems for which performance and cost are highly sensitive to individual components present in the waste stream (e.g., activated sludge and chemical oxidation), only limited data or data from somewhat different applications are generally available. The limitations in the data of this type are twofold. First, the characteristics of the treated waste streams in related applications of the subject controls are often known only in terms of major constituents, gross parameters, or classes of substances. Little may be known about specific organics, trace elements, or general toxic properties. Secondly, the performance characteristics of many controls are uncertain for some of the specific waste streams addressed in this PCTM even for the major constituent and gross properties. Key data sources and bases for performance and cost estimates for example controls discussed in conjunction with unique waste streams in Section 4 are summarized in Tables 5-2 through 5-4.

A data gap or limitation which exists for essentially all pollution control technologies relates to reliability. Because most of the potentially applicable pollution control technologies have not been employed in coal gasification/indirect liquefaction facilities, few directly related reliability data are available. Further, the overall characteristics and variability of waste streams in coal conversion facilities are often sufficiently different from those encountered in other industries that reliability data accumulated in other industries may not be applicable to coal conversion processes. These are particularly significant considerations with respect to wastewater treatment technologies and, to a lesser extent, hold for gaseous and solid waste control technologies also. It should be noted, however, that such data gaps cannot be addressed for specific controls prior to the application of these controls to coal conversion waste streams.

With regard to the products and by-products produced in K-T based liquefaction facilities, most of the physical and chemical properties reported are estimates relating to conceptual designs of commercial scale facilities. Despite the fact that the Fischer-Tropsch (F-T) process is applied commercially in South Africa, detailed chemical analysis data are not publicly available for F-T products. Detailed chemical analyses are not available for Mobil M-gasoline or coal-derived methanol, which are not currently produced on a commercial scale. Also, there are no chemical characterization data available for by-product sulfur from indirect liquefaction facilities. The data sources and bases for characterization estimates, data gaps and limitations, and research needs relating to products and by-products produced in K-T indirect liquefaction facilities are summarized in Table 5-5, at the end of this section.

TABLE 5-1. COMPLETED AND ONGOING DATA ACQUISITION PROGRAMS AT COAL GASIFICATION FACILITIES SPONSORED OR CO-SPONSORED BY THE EPA

Facility	Information Classification	Coal Used	Products
Medium/High Btu Gasification and Indirect Liquefaction Facilities (Foreign)			
● Lurgi Gasification			
- Kosovo, Yugoslavia	Data acquisition	Lignite	Medium Btu gas
- SASOL, S.A.	Plant visit and discussions	Low rank bituminous	Various via indirect liquefaction
- Westfield, Scotland	Plant visit and discussions	Various	Test center
● Koppers-Totzek Gasification			
- Modderfontein, S.A.	Data acquisition	High volatile "B" bituminous	Ammonia, methanol
- Ptolemais, Greece	Data acquisition (TVA & EPA)	Ill. No. 6 bituminous	Ammonia
- Kutahya, Turkey	Plant visit and discussions	Lignite	Ammonia
● Winkler Gasification			
- Kutakya, Turkey	Plant visit and discussions	Lignite	Ammonia
● Texaco Gasification			
- Federal Republic of Germany	Data acquisition (EPRI, TVA & EPA)	Ill. No. 6 bituminous	Test center
Low-Btu Gasification Facilities (U.S.)			
● Wellman Galusha			
- Site No. 1	Data acquisition	Anthracite	Fuel gas
- Site No. 2	Data acquisition	Lignite	Test center
● Chapman/Wilputte	Data acquisition	Low sulfur bituminous	Fuel gas
● Riley	Data acquisition	Lignite	Test
● Stoic (Foster Wheeler)	Data acquisition (DOE & EPA)	Western bituminous	Fuel gas
Control Research Facilities			
● Raw/Acid Gas Cleanup (Fluidized Bed Gasifier)	North Carolina State Univ.	Various	Test center
● Wastewater Treatability Studies	Univ. of North Carolina	Various	Test center
● Pollutant Identification (Bench Scale Gasifier)	Research Triangle Institute	Various	Test center
● Ash Leaching Evaluations	University of Illinois	Various	Test center
Other Domestic Facilities			
● Texaco Gasification			
- Ammonia from coal plant, TVA	Data acquisition (TVA & EPA)	Ill. No. 6 bituminous (in shakedown)	Ammonia
● Rectisol Acid Gas Cleanup	Texaco, Wilmington, CA	Oil fired partial oxidation	Process hydrogen

TABLE 5-2. DATA GAPS AND RESEARCH NEEDS - GASEOUS MEDIUM

Key for Technology Status and Data Sources

Technology Status

A. Commercial application in a K-T gasification facility
B. Bench scale or pilot testing
C. Technology transfer from another industry - similar but not identical streams
D. Conceptual

Data Source/Location

1. AECI Limited, Modderfontein, South Africa
2. Nitrogenous Fertilizer Industry, S.A., Ptolemais, Greece
3. Technology transfer from related industries
3A. Petroleum refining/petrochemical production
3B. Coke production
3C. Electric power generation
3D. Natural gas processing
3E. Municipal waste treatment
4. Conceptual or proposed design/engineering studies
5. Vendor supplied information

Data Source and Basis	Data Gaps/Limitations	Research Needs
Uncontrolled Primary Waste Streams H$_2$S-Rich Offgas (Stream 216)		
Offgas composition is based upon selective Rectisol performance data from commercial K-T coal gasification at AECI Limited, Modderfontein, South Africa and from several commercial oil partial oxidation units. H$_2$S to COS ratios in raw gas are also substantiated by commercial scale gasification tests with an Illinois No. 6 coal at the Nitrogenous Fertilizers Industry, S.A., Ptolemais, Greece. Status: A, C Data Sources: 1, 2, 3A, 5 PCTM References: Sections 3.3.6, 4.1.1.1, 4.1.1.5, and Appendix D.	The selectivity of acid gas removal is dependent upon several design factors; however, available data indicate that selective Rectisol can economically produce an H$_2$S-rich offgas containing at least 25% total sulfur for a wide range of feed coal sulfur contents. Relative quantities of sulfur species in raw gas, and therefore in the H$_2$S-rich offgas, may differ somewhat for different rank coals.	Verification of sulfur and minor constituent characterization data in U.S. facilities is desirable.
Sour Gas from Cyanide Wash Flash (Stream 214)		
Flash gas compositions have been estimated from gas solubility data. Status: D Data Sources: 4 PCTM References: Sections 3.3.4, 4.1.1.2, and 4.1.1.5	No waste gas generation or characterization data are available.	Generation rate and characterization data are needed to define applicable control alternatives.

(Continued)

TABLE 5-2. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Control Techniques **Claus Bulk Sulfur Removal**		
Performance and cost estimates are based upon data from applications in coke plants, oil refineries, and gas processing plants. Although no data are available for coal gasification applications, data from other applications cover the range of all constituents encountered in K-T coal gasification. Status: C Data Sources: 3A, 3B, 3D, 5 PCTM References: Sections 4.1.1, 4.1.1.1, and 4.1.1.5	Performance, cost, and reliability data in coal gasification applications are not available.	Performance, cost, and reliability data should be obtained for K-T coal gasification applications.
Secondary Waste Streams		
Spent catalyst is the principal secondary waste stream from Claus.	Spent catalyst generation rates and characteristics are not accurately known.	Generation rate and characterization data are needed to define applicable control alternatives. Such data may be obtainable from Claus plant operators in related industries.
Beavon/Stretford Tail Gas Treatment		
Performance and cost estimates are based upon data from treatment of Claus plant tail gases with low CO_2 feed composition from petroleum refinery applications. Status: C Data Sources: 3A PCTM References: Sections 4.1.1, 4.1.1.1, and 4.1.1.5	Uncertainties relate to performance of the catalytic hydrogenation section and the operability of the Stretford sulfur recovery section in high CO_2 applications. Process costs as a function of both volumetric flow and sulfur loadings are not accurately known.	The operability, performance, and cost of Beavon/Stretford tail gas treatment in high CO_2 applications should be determined.
Secondary Waste Streams		
• Sour Condensate	Condensate characteristics, particularly with respect to $S^=$, CN^-, and NH_4^+ are not available.	Condensate characteristics should be determined to define pollution control alternatives. Appropriate data may be obtainable from licensors or operators of refinery units.
• Stretford Solution Purge	Limited characterization data are available. Purge rates in high CO_2 applications are unknown. Reductive incineration of solution purge has not been demonstrated at commercial scale.	Purge generation rates and characteristics should be determined in coal gasification facilities when the technology is applied commercially. Characterization, performance, and cost data for reductive incineration should be obtained when the process is applied commercially.
• Stretford Oxidizer Vent Gas	Characterization data are not available for oxidizer vent gas. However, in K-T coal gasification applications there are no gaseous components of environmental concern having potential for being present in the vent gas.	Oxidizer vent gas should be characterized in K-T coal gasification facilities when the technology is applied commercially.

(Continued)

TABLE 5-2. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Secondary Waste Streams (Continued)		
• Spent Beavon Catalyst	Spent catalyst generation rates and characteristics are not accurately known.	Characterization data are needed to define applicable control/resource recovery alternatives. Appropriate data may be obtainable through licensors or operators of refinery units.
SCOT Tail Gas Treatment		
Performance and cost estimates are based upon data from treatment of Claus plant tail gases with low CO_2 feed compositions from petroleum refinery applications. Status: C Data Sources: 3A, 5 PCTM References: Sections 4.1.1, 4.1.1.1, and 4.1.1.5	Uncertainties relate to performance and cost in high CO_2 applications. SCOT units are used in high CO_2 applications in natural gas processing although associated performance and cost data are not currently available.	SCOT performance in high CO_2 applications should be determined. Units in gas plant applications are best suited for demonstrating applicability to K-T coal gasification facilities.
Secondary Waste Streams		
• Sour Condensate	Condensate characteristics, particularly with respect to $S^=$, CN^-, and NH_4^+ are not available.	Condensate characteristics should be determined to define pollution control alternatives. Appropriate data may be obtainable through licensors or operators of refinery units.
• Spent SCOT Catalyst	Spent catalyst generation rates and characteristics are not accurately known.	Characterization data are needed to define applicable control/resource recovery alternatives. Appropriate data may be obtainable through licensors or operators of refinery units.
Wellman-Lord (W-L) Tail Gas Treatment		
Performance and cost estimates are based upon data from refinery and power plant applications. Status: C, D Data Sources: 3A, 3C, 4, 5 PCTM References: Sections 4.1.1, 4.1.1.1, and 4.1.1.5	Since W-L feed gas is incinerated, and the absorption solution is not affected by CO_2 concentration, data from existing units should be directly transferable to K-T coal gasification applications. Effects of volumetric flow rate and sulfur loading on cost are uncertain.	None
Secondary Waste Streams		
o Sour Condensate	Limited characterization data are available	Additional characterization data are desirable
o Thiosulfate/Sulfate By-Product Purge	Limited generation rate and characterization data are available	Additional generation rate and characterization data are desirable.

(Continued)

TABLE 5-2. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Thermal Incineration **Performance and cost estimates are based upon data from waste gas and liquid waste incineration applications.** **Status:** C **Data Sources:** 3A, 3B, 3C, 3D **PCTM References:** Sections 4.1.1, 4.1.1.1, and 4.1.1.5	Uncertainties relate primarily to the operability of and emissions from incinerators with feed gases having high CO_2 levels and low heating valves.	Applicable data on operability of and emissions from incinerators may be obtainable from operators of refinery units or gas plants.
Uncontrolled Primary Waste Stream CO_2-Rich Offgas (Stream 219)		
Offgas total sulfur and CO concentrations are based upon selective Rectisol performance data from commercial K-T coal gasification at AECI Limited, Modderfontein, South Africa and from several commercial oil partial oxidation units. Design modifications discussed in conjuntion with control of CO emissions are based on licensor inputs. Status: A, C Data Resources: 1, 3A, 5 PCTM References: Sections 3.3.6 and 4.1.1.2	Baseline offgas characterization data, and specifics of CO moderating Rectisol design modifications and associated performance in indirect coal liquefaction facilities are not available.	Offgas characteristics in indirect coal liquefaction facilities should be determined. It appears likely that two streams would require characterization: (1) a CO_2-rich vent gas, and (2) a CO-rich waste gas.
Control Technology Catalytic Incineration Performance and cost estimates are based upon data from industrial waste gas incineration applications. Status: C Data Sources: 3A PCTM References: Sections 4.1.1 and 4.1.1.3	Available data on performance and cost are limited.	Performance and cost data for waste streams similar to those produced in K-T coal gasification facilities should be obtained.
Uncontrolled Primary Waste Stream Fugitive Organic Emissions from Process Equipment (Stream 241)		
Emission estimates for fugutive organic emissions from leaking process equipment were based on emission factors for these components for conventional petroleum refining process equipment. Component counts were based on plot plans for potential K-T based synthetic fuel plants. Status: C Data Sources: 3A PCTM References: Sections 3.7.1 and 4.1.5	Characterization data are not available for synthetic liquids or their vapors.	Exact composition of vapors for synthetic fuel plant process equipment may differ from petroleum refinery process equipment; however, the control technology that is applicable is not likely to be affected by these characteristics. Since these emissions directly enter the atmosphere, additional information on specific constituents of the vapor may be desirable.

(Continued)

TABLE 5-2. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Control Technologies Leak Detection and Repair Methods		
Leak detection and repair methods have been successfully used to control fugitive organic emissions from petroleum refining equipment. This technique was assumed to be applicable to indirect liquefaction process equipment. Emission estimates were based upon emission factors developed from test data for petroleum refining process equipment.	The performance of leak detection and repair methods are not expected to be different for K-T based synthetic fuel plants.	Research needs relate to characterization of the emissions and not to the controls.
Status: C Data Sources: 3A PCTM References: Sections 4.1.5 and 4.1.5.2		
Equipment Specification		
Replacement of leaking equipment with leakless components has been successfully used for the control of fugitive organic emissions from petroleum refining equipment. This technique was assumed to be applicable to indirect liquefaction process equipment. Emission estimates were based upon emission factors developed from test data for petroleum refining process equipment.	The performance of equipment specification is not expected to be different for K-T based synthetic fuel plants.	Research needs relate to characterization of the emissions and not to the controls.
Status: C Data Sources: 3A PCTM References: Sections 4.1.5 and 4.1.5.2		
Uncontolled Primary Waste Stream Storage Emissions (Streams 308 to 313)		
Emission estimates were based upon emission factors developed from test data for conventional petroleum liquid storage. The amount and type of liquids stored were determined from the synthesis process used. Liquids with vapor pressure greater than 10 kPa were assumed to be stored in floating roof tanks. Low vapor pressure liquids were assumed to be stored in fixed roof tanks.	Characterization data are not available for synthetic liquids or their vapors.	Exact composition of vapors from synthetic fuel storage may differ from those of conventional petroleum liquids; however, the control technology that is applicable is not likely to be affected by these characteristics. Since these emissions directly enter the atmosphere, additional information on specific constituents of the vapor may be desirable.
Status: C Data Sources: 3A PCTM References: Sections 3.6.5 and 4.1.5		

(Continued)

TABLE 5-2. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Control Technology Secondary Seals on Floating Roof Tanks		
Since secondary seals are used to control evaporative emissions from floating roof tanks storing petroleum liquids, they were assumed to be applicable to storage tanks containing synthetic liquids. Emission estimates were based upon emission factors developed from test data for petroleum liquids storage. Status: C Data Resources: 3A PCTM References: Section 4.1.5	The performance of secondary seals is not expected to be different for synthetic liquid storage tanks.	Research needs relate to characterization of the emissions and not to the controls.
Internal Floaters or Fixed Roof Tanks		
Since internal floaters are used to control evaporative emissions from fixed roof tanks storing petroleum liquids, they were assumed to be applicable to storage tanks containing synthetic liquids. Emission estimates were based upon emission factors developed from test data for petroleum liquids storage. Status: C Data Sources: 3A PCTM References: Section 4.1.5	The performance of internal floaters is not expected to be different for synthetic liquid storage tanks.	Research needs relate to characterization of the emissions and not to the controls.

TABLE 5-3. DATA GAPS AND RESEARCH NEEDS - AQUEOUS MEDIUM

Key For Technology Status and Data Sources

Technology Status	Data Source/Location
A. Commercial application in a K-T gasification facility	1. AECI Limited, Modderfontein, South Africa
B. Bench or pilot scale testing	2. Nitrogenous Fertilizer Industry, S.A., Ptolemais, Greece
C. Technology transfer from another industry - similar but not identical streams	3. Technology transfer from related industries
D. Conceptual	3A. Petroleum refining/petrochemical production
	3B. Coke production
	3C. Electric power generation
	3D. Natural gas processing
	3E. Municipal waste treatment
	4. Conceptual or proposed design/engineering studies
	5. Vendor supplied information

Data Source and Basis	Data Gaps/Limitations	Research Needs
Uncontrolled Primary Waste Streams Cooling and Dust Removal Blowdown (Stream 210)		
Blowdown composition is based upon data from commercial scale gasification tests with an Illinois No. 6 coal at the Nitrogenous Fertilizers Industry, S.A. Ptolemais, Greece. Halide concentrations were adjusted consistent with coal Cl^- and F^- contents. Status: A, D Data Sources: 2, 4 PCTM References: Sections 3.3.1 and 4.2.3.3	Available characterization data are limited to gasification of one U.S. bituminous coal and several foreign sub-bituminous coals and lignites. However, the quantity and quality of blowdown are highly dependent upon coal characteristics and design specifics. Data from gasification of foreign coals reflects designs which are not being proposed for use in the U.S.	The existing data base adequately defines ranges of the primary parameters of concern (eg CN^-, SCN^-, NH_4^+ and TDS). However, these data should be verified in U.S. facilities.
Primary Compression and Cooling Condensate (Stream 211)		
Condensate flow rate and NH_4^+, Cl^-, and F^- concentrations have been estimated based upon washer cooler performance during commercial scale gasification tests with an Illinois No. 6 coal at the Nitrogenous Fertilizer Industry, S.A., Ptolemais, Greece. Other parameters are based upon condensate characterization data from commercial K-T gasification at AECI Limited which gasifies South African sub-bituminous coal. Status: A, D Data Sources: 1, 2, 4 PCTM References: Sections 3.3.2 and 4.2.3.2	Condensate characterization data are available only from AECI Limited, and reflect one coal and one washer cooler design.	Further characterization of this stream may be of limited value due to its low flow rate relative to similar process streams (e.g., cooling and dust removal blowdown).

(Continued)

TABLE 5-3. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Cyanide Wash Water (Stream 215)		
The flow rate of cyanide wash water is based upon nominal flow rate data from AECI Limited at Modderfontein, South Africa. Wash water composition has been estimated from gas solubility data. Status: A, D Data Sources: 1, 4 PCTM References: Sections 3.3.4 and 4.2.3.1	No characterization data are available.	Characterization with respect to CN^-, SCN^- and $S^=$ is desirable for defining control processes and costs.
Synthesis Wastewaters - Mobil M (Stream 233), F-T (Stream 223), and Methanol Synthesis (Stream 236) Condensate		
Characterization and flow estimates are from conceptual designs and from data on product/compound production rates. Fischer-Tropsch estimates reflect commercial scale operating data, while Mobil M-gasoline estimates reflect pilot scale data. Methanol estimates are from engineering/cost studies rather than direct test data. Status: B, D Data Sources: 4 PCTM References: Sections 3.4 and 4.2.2	Uncertainties relate to both the extent to which by-product organics would be reclaimed within the upgrading operation and the exact species which are present in the waste. The biodegradabilities of these wastes are also not established.	Actual characterization data may be obtained from SASOL (F-T) and from existing methanol plants. Mobil M data will have to await the construction of the first commercial plant.
Control Technologies Filtration		
Removal of suspended solids is based on performances realized in parallel applications, particularly the petroleum refining industry. Actual performance will depend on the characteristics of the filter media and the characteristics of the suspended solids, including particle size distribution and tendency to agglomerate. Costs are based on vendor quotes. Status: C Data Sources: 3A, 3E, 5 PCTM References: Sections 4.2.1.1, 4.2.2.1, 4.2.3.1, 4.2.3.2 and 4.2.4	Performance has not been determined for the K-T wastewaters.	Existing experience from application of filtration to parallel industries is sufficient to estimate performance to within reasonable limits of accuracy. More refined estimates would have little bearing on the applicability of this control technology.

(Continued)

TABLE 5-3. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Polysulfide Addition		
Conversion of cyanide to thiocyanate is based on the results of EPA-sponsored preliminary kinetic studies. There exists no known precedent for effecting the conversion as the basis of a water pollution control process, although polysulfide is commonly added at key process points in petroleum refineries to control cyanide-induced corrosion. Capital costs are based on those requirements for chemical addition processes such as chemical oxidation and disinfection. Operating costs are dominated by chemical requirements, estimated from both stoichiometric and kinetic characteristics of the polysulfide reaction. Status: B, C, D Data Sources: 3A, 4 PCTM References: Section 4.2.1.4, 4.2.3.1 and 4.2.4	(1) Optimal conditions for the polysulfide reaction are not known, particularly the pH dependence and the influence of chemical species other than cyanide and thiocyanate.	(1) The affect of residual polysulfide on downstream processes and its amenability to removal by sedimentation or filtration needs to be determined. In particular, since a biological treatment process may well follow polysulfide addition, research is needed to determine the fate of residual polysulfide in an activated sludge system and its affect on the microorganisms.
	(2) Residual polysulfide is expected to precipitate at near neutral pH, posing possible problems for downstream control processes. Characteristics of this precipitate including its settleability and filterability are not known.	(2) Laboratory tests are needed to more fully define the reaction for varying conditions of pH, temperature, and concentrations of cyanide and other species. Experience in the petroleum refining industry combined with the results of preliminary studies indicate that the reaction occurs at a greatly increased rate when the polysulfide is added as ammonium polysulfide rather than sodium polysulfide. New research efforts should consider this.
	(3) The feasibility of identifiable methods of adding polysulfide to the wastewater is not known. In particular, it may prove feasible to add polysulfide directly to the cyanide wash on the gas cooling/dust removal circuit.	(3) Research is needed to determine the feasibility of accomplishing the cyanide conversion in conjunction with some other process, whether that be some other water pollution control process or a part of the base plant. Likely possibilities include addition of polysulfide to the cyanide wash or the gas cooling/dust removal circuit, to an ion exchange column, or to an activated sludge system.
Activated Sludge - Removal of Organics		
Removal of dissolved organics are expected to exceed that typically realized in parallel applications since only simple, highly biodegradable organics are involved. Actual performance will be specific to the exact characteristics of the wastewater. Costs are based on values reported in the literature, appropriately scaled on the basis of system loading. Status: B, C, D Date Sources: 3A, 3B, 3E, 4 PCTM References: Section 4.2.1.5, 4.2.2.1, and 4.2.4	(1) Performance has not been determined for the K-T wastewaters. Only by direct testing of the wastewater to be treated can the performance of an activated sludge system be determined with certainty. (2) The partitioning of cyanide between that biodegraded, that stripped from solution, and that escaping in the effluent is not known. Several studies in the open literature report cyanide as being biodegradable when it occurs as part of a large matrix of organic species, but removals vary widely. Similar unknowns exist for sulfide.	The fate of cyanide and sulfide in the activated sludge system needs to be determined. The biodegradability of cyanide in particular is highly dependent on the particular microorganisms that are held in the activated sludge reactor. Since the characteristics of these microorganisms are specific to the characteristics of the wastewater being treated, it is necessary to evaluate the cyanide and sulfide species in a system treating either an exact sample of the wastewater or one very carefully synthesized.

(Continued)

TABLE 5-3. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Activated Sludge - Removal of Thiocyanate and Ammonia		
Removal of thiocyanate and ammonia from wastewaters containing essentially no organics is based on performance recorded in the literature and the results of a laboratory scale study. Costs are based on values reported in the literature, appropriately scaled on the basis of system loading. Status: B, C, D Data Sources: 3E, 4 PCTM References: Sections 4.2.1.4, 4.2.3.1, 4.2.3.2, and 4.2.4	Performance has not been determined for the K-T wastewaters.	Bench-scale studies using actual or synthetic wastewaters could better assess the performance and requirements of this system. Commercial scale performance should be determined when U.S. facilities become fully operational.
Biological Denitrification		
Removals of nitrate are based on performances typically realized in parallel industries and municipal applications. Costs are based on values reported in the literature, appropriately scaled on the basis of system loading. Status: B, C, D Data Sources: 3E, 4 PCTM References: Sections 4.2.1.4, 4.2.3.1, 4.2.3.2, and 4.2.4	Performance has not been determined for the K-T wastewaters.	Bench-scale studies using actual or synthetic wastewaters could better assess the performance and requirements of this system. Commercial scale performance should be determined when U.S. facilities become fully operational.
Clinoptilolite-based Ion Exchange		
Removal of ammonia is based on the results of EPA-sponsored, preliminary laboratory scale studies using a synthetic wastewater having an ammonia concentration representative of that expected in the K-T wastewater. Costs are based on values reported in the literature for two plants treating municipal-strength wastewaters: the Upper Occoquan plant (Virginia) and the South Lake Tahoe plant (California). Costs are extrapolated on the basis of ammonia loading. Status: B, C, D Data Sources: 3E, 4 PCTM References: Sections 4.2.4, 4.2.3.1, 4.2.3.2, and 4.2.4	Performance has not been determined for the K-T wastewaters. Since all existing clinoptilolite-based ion exchange systems are designed to treat municipal-strength wastewaters, little is known about the cost characteristics of a system designed to treat the higher ammonia loadings associated wtih the K-T wastewaters.	Preliminary studies need to be supported by a more comprehensive effort. Research should be directed toward determining feasibility of the process by concentrating on the following areas of study: maximum period of operating cycle, ammonia leakage during loading as a function of residence time, regeneration requirements of the clinoptilolite resin (including attrition), affects of reduced sulfur and other reduced nitrogen species on the resin, and possible changes in species other than ammonia passing through the bed. Information accumulated by operating systems needs to be assembled and then applied to K-T-related systems. Areas of information would include more detailed cost data and operating experience with regeneration equipment.

(Continued)

TABLE 5-3. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Activated Carbon Adsorption		
Removals of all pollutants are based on data from the refining and by-product coking industries. Actual removal efficiencies will depend on pH, molecule size, and structure of the organics present in the wastewater. Costs are based on data from the refining and by-product coking industries, extrapolated on the basis of COD loading. Status: B, C Data Sources: 3A PCTM References: Sections 4.2.1.6, 4.2.2.1 and 4.2.4	Performance has not been determined for the K-T wastewaters.	Laboratory or pilot scale tests are needed on the K-T wastewaters. While many of the individual chemical species determining COD are known, the performance cannot be synthesized from performances typical for individual species. Performance is generally specific to the wastewater being treated and therefore must be determined on an individual case basis.
Chemical Oxidation		
Removals are based on the chemical oxidation amenability of individual species in the wastewater. Costs are based on data available in the open literature. Status: B, C, D Data Sources: 3A, 3E, 4 PCTM References: Sections 4.2.1.6, 4.2.3.1, 4.2.3.2, and 4.2.4	No experience exists for testing the K-T wastewater. Overall pH dependence and general reactor requirements are not known. For wastewaters where organics are present, removals are uncertain, and unknown chemical species not present in the influent are likely to be found in the effluent.	Testing of the K-T wastewaters on a scale larger than laboratory scale is needed to better assess treatability. Destruction of chemical species by chemical oxidation under carefully controlled conditions are not necessarily realized in a full scale process.
Thermal Oxidation		
Destruction of organics is based on that realized in other industries where organics, sometimes much more refractory than those in the K-T wastewaters, are removed. Costs are based on vendor quotes. Status: C Data Sources: 3A, 3B, 5 PCTM References: Sections 4.2.1.6, 4.2.2.1 and 4.2.4	Performance has not been determined for the K-T wastewaters.	Additional research is not likely to improve the present data base. Considerable research has been completed in recent years, particularly in the area of destroying organics regarded as hazardous. The capabilities and limitations of the process are thereby well established.
Cooling Tower Concentration		
All chemical species with exception of ammonia and sulfide are assumed to be concentrated into the blowdown stream without losses due to volatilization or drift. Status: D Data Sources: 4 PCTM References: Sectons 4.2.1.7, 4.2.2.1, 4.2.3.1, 4.2.3.2 and 4.2.4	Performance has not been determined for the K-T wastewaters. Loss of volatile species and potential for corrosion are not known.	Regardless of research, the feasibility of cooling tower concentration would be determined on an individual case basis. Commercial scale performance should be evaluated in fully operational U.S. facilities.

(Continued)

TABLE 5-3. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Forced Evaporation		
All chemical species with the exception of ammonia and sulfide are assumed to be concentrated into the blowdown stream without losses due to volatilization. Costs are based on vendor quotes. Status: D Data Sources: 4, 5 PCTM References: Sections 4.2.1.7, 4.2.2.1, 4.2.3.1, 4.2.3.2 and 4.2.4	Performance has not been determined for the K-T wastewaters. The concentration of individual chemical species that will be carried over into the evaporator overhead is not known. Extent of corrosion potential is not known.	Unknowns are not expected to have a significant impact on the applicability of this process. However, performance should be evaluated in fully operational U.S. facilities.

TABLE 5-4. DATA GAPS AND RESEARCH NEEDS - SOLID MEIDUM

Key For Technology Status and Data Sources

Technology Status	Data Source/Location
A. Commercial application in a K-T gasification facility	1. AECI Limited, Modderfontein, South Africa
B. Bench or pilot scale testing	2. Nitrogenous Fertilizer Industry, S.A., Ptolemais, Greece
C. Technology transfer from another industry - similar but not identical streams	3. Technology transfer from related industries
D. Conceptual	3A. Petroleum refining/petrochemical production
	3B. Coke production
	3C. Electric power generation
	3D. Natural gas processing
	3E. Municipal waste treatment
	4. Conceptual or proposed design/engineering studies
	5. Vendor supplied information

Data Source and Basis	Data Gaps/Limitations	Research Needs
Uncontrolled Primary Waste Streams Quenched Slag (Stream 207)		
Slag generation rates, leachability data and residual moisture are based upon commercial scale gasification of an Illinois No. 6 coal at the Nitrogenous Fertilizers Industry, S.A. in Ptolemais, Greece. Contaminants in the residual moisture have been estimated assuming a common slag quench/washer cooler water circuit, without slag rinsing.	Slag/dust ash partitioning and slag leachability data are not available for other bituminous coals or lower rank coals.	Slag/dust partitioning and slag leachability data for other bituminous coals and lower rank coals should be determined. Partitioning data for various ranks of foreign coals may be obtainable through licensors/operators.
Status: A, D Data Sources: 2, 4 PCTM References: Sections 3.2.1 and 4.3.2.1		

(Continued)

TABLE 5-4. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Dewatered K-T Dust (Stream 209)		
The composition of dry K-T dust and the associated liquids are based upon data from commercial scale gasification of Illinois No. 6 coal at the Nitrogenous Fertilizers Industry, S.A. in Ptolemais, Greece. A nominal dewatered dust moisture content has been assumed consistent with that indicated in a conceptual design for a sub-bituminous coal based hydrogen production facility. Status: A, D Data Sources: 2, 4 PCTM References: Sections 3.2.1 and 4.3.2.1	Slag/dust ash partitioning data, dust carbon and sulfur contents, and dust leachability data are not available for other bituminous coals or lower rank coals. Dust dewatering data and structural stability data are not available.	Slag/dust ash partitioning data, dust carbon and sulfur contents, and dust leachability data for other bituminous coals and lower rank coals should be determined. Partitioning and dust characterization data for various ranks of foreign coals may be obtainable through licensors/operators. Dust dewatering data should be obtained for a range of coal types. Engineering and geotechnical data are needed to establish design data for land-based disposal techniques.
Control Technologies Resource Recovery		
Reuse as Construction Material		
Potential alternatives for recycling the gasifier slag are based upon current practices for ash from coal-fired power plants. Status: C Data Sources: 3C PCTM Reference: Section 4.3.2.1	The available market for recycling the slag is uncertain.	The availability of market is highly dependent upon local conditions which can only be assessed on a site-by-site basis.
Fluidized Bed Combustion of Dust		
The burning of K-T dust in a fluidized bed combustion (FBC) boiler is based upon an approach under consideration for a proposed K-T plant in Alabama and an existing K-T plant in Modderfontein, South Africa. Status: B, D Data Sources: 1, 4 PCTM Reference: Section 4.3.2.1	(1) The viability of commercial scale FBC boiler using dewatered K-T dust as fed has not been proven. (2) Although there are cost data for coal-fired FBC units, these data may not apply to combustion of high moisture and ash K-T dust.	The viability of FBC with K-T dust should be determined. Data might be obtainable through AECI Limited which is currently evaluating this alternative.
Secondary Waste Streams		
o FBC Boiler Ash	No leachability data are available.	The leachability data should be determined for range of coal types.
o Spent FBC Boiler Bed Sorbent	The flow rate and the leachability of this material is not known.	The flow rate and the leachability of this material might be obtained from AECI.

(Continued)

TABLE 5-4. (Continued)

Data Source and Basis	Data Gaps/Limitations	Research Needs
Landfill		
Landfilling of the waste is based upon current practices in the electric utility industry and other industries. Status: C Data Sources: 3C PCTM Reference: Section 4.3.2.1	The long term leachate generation rates and characteristics are not known, and the compatibility and long term performance of landfill liners have not been established.	Long term column or landfill cell studies are needed to characterize the leachate and to determine liner performance. Appropriate materials for these tests may not be available until the first K-T plant is constructed in the U.S. Also, since these are long term studies the data may not be available in time to influence facility designs that are currently in advanced stages.
Surface Impoundment		
Disposal of waste in surface impoundments is based upon current practices in the electric utility industry and other industries. Status: C Data Sources: 3C PCTM Reference: Section 4.3.2.1	Same as landfill.	Same as landfill.
Fixation		
Fixation of the K-T dust to improve its structural stability and leachability characteristic is based on current practices for FGD sludge and other industrial wastes. Status: C Data Sources: 3C PCTM References: Section 4.3.2.1	Performance and cost for the application are not known.	Treatability studies with various chemical additives should be performed to determine the technical and economic feasibility of this approach.

TABLE 5-5. DATA GAPS AND RESEARCH NEEDS - PRODUCTS/BY-PRODUCTS

Key for Technology Status and Data Sources

Technology Status	Data Sources
A. Commercial application in a K-T gasification facility	1. AECI Limited, Modderfontein, South Africa
B. Bench scale or pilot testing	2. Nitrogeneous Fertilizer Industry, S.A., Ptolemais, Greece
C. Technology transfer from another industry - similar but not identical streams	3. Technology transfer from related industries
D. Conceptual	3A. Petroleum refining/petrochemical production
	3B. Coke production
	3C. Electric power generation
	3D. Natural gas processing
	3E. Municipal waste treatement
	3F. Methanol production
	4. Conceptual or proposed design/engineering studies
	5. Vendor supplied information

Data Source and Basis	Data Gaps/Limitations	Research Needs
Fischer-Tropsch Synthesis Products Gasoline, Diesel Oil, Heavy Oil, Alcohols, LPG and SNG (Streams 100 through 107)		
Production rates and composition estimates are based upon conceptual designs for commercial scale F-T facilities. Status: D Data Sources: 4 PCTM References: Sections 3.4.2 and 3.5.2	Characterization, storage stability, and use data for F-T products are limited. The influence of synthesis process variables on product characteristics is unknown; storage stability, intermediates processability, and consumption/utilization characteristics are similarly largely unknown.	Detailed characterization data are desirable. Environmental effects associated with fugitive and evaporative emissions and product utilization should be determined. Such effects should be evaluated relative to environmental effects associated with analog petroleum products.
Methanol Synthesis Product Fuel Grade Methanol (Stream 108)		
Production rates are based upon conceptual designs for commercial scale methanol facilities. Composition estimates are based upon conceptual designs and analyses of methanol produced from petroleum feedstocks. Source: C, D Data Sources: 3F, 4 PCTM References: Sections 3.4.1 and 3.5.1	Characterization data for methanol from indirect coal liquefaction are limited. The influence of synthesis process variables on product methanol characteristics is unknown.	The EPA Office of Pesticides and Toxic Substances has declared that methanol, regardless of source, is methanol and does not require Premanufacturing Notices for the production of coal-based methanol. On this basis, no research effort is required.
Mobil M-gasoline Synthesis Products Gasoline, Mixed Butanes, and Propane (Streams 109, 110, and 111)		
Production rates and composition estimates are based upon conceptual designs of commercial scale Mobil M-gasoline facilities. Status: D Data Sources: 4 References: Sections 3.4.4 and 3.5.3	Characterization data for Mobil M-gasoline products are limited. The influence of synthesis process variables on product characteristics is unknown.	Detailed characterization data are desirable. Environmental effects assiciated with fugitive and evaporative emissions and product utilization should be determined. Such effects should be evaluated relative to environmental effects associated with analog petroleum products.
By-Products Sulfur from Claus and Stretford Process (Streams 403 and 408)		
Production rate estimates are based upon published control performance data and engineering estimates of waste gas sulfur contents. Status: C, D Data Sources: 3A, 3B, 3D, 4 References: Sections 4.1.1, 4.1.1.1 and 4.1.1.5	Essentially, no characterization data are available for Claus and Stretford sulfur.	Characterization of sulfur is desirable, particularly with respect to contaminants which influence sulfur marketability, and possible downstream processing for various purposes.

SECTION 6

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APPENDIX A

COSTING METHODOLOGY, BASES, AND ASSUMPTIONS

Capital and total annualized cost estimates were developed for uncontrolled Koppers-Totzek (K-T) based synfuels facilities and for pollution control processes in order to provide an indication of the economic impact of pollution controls. These estimates are based primarily on factored estimates of costs contained in non-proprietary published literature. As such, they should be viewed only as general indicators of expected costs and should not be construed as definitive cost estimates for a specific plant. All costs have been adjusted to a 1980 dollar basis using generally accepted cost indexes such as the Chemical Engineering (CE) plant cost annual index.

To the extent possible, the same methodology was used to develop capital and total annualized cost estimates for both the base plants and pollution controls. Details of these methodologies are presented in Sections A.1 and A.2, respectively. The bases for the base plant cost estimates are presented in Section A.3. Bases for the pollution control cost estimates are presented in the Pollution Control Appendices for the PCTM series.

A.1 CAPITAL COST ESTIMATING METHODOLOGY

Costs presented as capital costs or investments in the K-T PCTM are total depreciable investments (TDI). TDI includes:

1) purchased and delivered equipment costs;
2) labor and materials costs to install equipment;
3) indirect installation charges, such as
    - engineering and construction costs,
    - contractor fees, and
    - project and process contingency reserves, and;
4) interest expenses on capital spent prior to start of production (interest during construction).

A variety of methods can be used to estimate the above cost items, although most methodologies utilize a factored approach. In factored cost estimates, the cost of purchased and delivered equipment is obtained from vendor quotes or estimated from previous projects using similar equipment. The remaining cost items are then estimated as a "factor" times the purchased and delivered equipment costs or other subsequently derived subtotal.

For costs estimates developed for this PCTM, the major source of cost information was the open literature, although some vendor quotes were used. In general, literature cost information is not reported as delivered equipment costs: some data are published as installed equipment costs (purchased equipment plus direct installation costs), some include one or more of the indirect installation charges (listed previously), some are TDI estimates, and others are total capital investment requirements (TDI plus working capital and land costs).

In order to provide consistency in the various capital cost estimates required for the PCTM, a capital cost methodology was developed. The methodology (and cost factors) used are summarized in Table A-1. Most cost data obtained from the literature were installed equipment costs (IEC) which often included components such as piping, instrumentation, and substructures. As indicated in the table, indirect installation charges were estimated as 48% of the IEC. Adding the indirects to the IEC gave the total plant (or process) costs. Interest during construction (IDC) was estimated as 22.6% of the total plant costs. The total depreciable investment (TDI) is the sum of these two terms. Working capital (WC) for the base plant cost estimates has been assumed to be the value of a 60 day coal inventory. No provision for working capital related to pollution control equipment has been included. Summing the TDI and WC gives the total capital investment (TCI). It should be noted that the PCTM does not address a specific K-T synfuels facility or facility location, and thus the amount and value of associated land is unknown. Therefore, for cost estimating purposes, the cost of land has not been included in the total capital investment estimates presented.

TABLE A-1. CAPITAL COST ESTIMATING METHOD

Installed Equipment Costs (IEC)

Indirect Installation Costs (IIC)

- Engineering and Construction (25% of IEC)
- Fees (3% of IEC)
- Contingency (20% of IEC)

Total Plant Costs (TPC = IEC + IIC)

Interest During Construction (IDC = 22.6% of TPC)

Total Depreciable Investment (TDI = TPC + IDC)

Working Capital (WC = value of 60 day coal inventory for base plant cost estimates)

*Total Capital Investment (TCI = TDI + WC)

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*The PCTM does not address a specific K-T synfuels facility or facility location, and thus the amount and value of associated land is not unknown. Therefore, for cost estimating purposes the cost of land has not been included in total capital investment estimates presented in this PCTM.

A.2 ANNUALIZED COST ESTIMATING METHODOLOGY

Annualized costs consist of annual operating expenses plus annualized capital-related charges. Annual operating expenses include costs for labor (operating, supervision, and maintenance), raw materials, chemicals, catalysts, utilities (steam, electricity, cooling water, etc.), and overhead. Capital-related charges include interest on working capital, local taxes, insurance, depreciation, income taxes, and return on investment. The unit costs or factors used to estimate total annualized costs in this PCTM are listed in Table A-2. All of the terms listed in Table A-2, except capital recovery, are expressed in first year costs (i.e., in constant 1980 dollars). The capital recovery, however, is a levelized value calculated using standard present worth and levelized cost procedures and the economic assumptions listed in Table A-3.

TABLE A-2. UNIT COSTS AND FACTORS FOR ANNUALIZED COST ESTIMATES

- Operating Labor ($11/hr)
- Supervision (15% of operating labor)
- Maintenance (2% of total depreciable investment)
- Maintenance Supervision (5% of maintenance)
- Raw Illinois No. 6 Coal ($35.44/Mg)
- Raw Water ($0.031/m^3)
- Utilities
  - Steam ($6.30 to $9.10/Mg depending on quality)
  - Electricity ($0.033/kW-hr)
  - Fuel Gas ($1.79/GJ)
  - Cooling Water ($0.08/m^3)
  - Boiler feed water ($0.264/m^3)
- Chemicals and Catalysts (representative early 1980 costs)
- Overhead Charges
  - Plant overhead (50% of operating labor)
  - General and administrative overhead (15% of operating labor and maintenance)
- Laboratory Charges (5% of operating labor)
- Capital Related Charges
  - Interest on working capital (12% of working capital)
  - Local taxes and insurance (3.5% of total depreciable investment)
  - Capital recovery, including income taxes, depreciation, and profit (13.7% of total depreciable investment)

TOTAL ANNUALIZED COSTS (summation of above items)

TABLE A-3. ASSUMPTIONS USED TO CALCULATE CAPITAL RECOVERY FACTOR

Financing basis:	100% equity
Desired after tax return on investment:	12% of total depreciable investment
Income tax rate:	48% of taxable income
Economic facility life:	20 years
Facility life for depreciation purposes:	16 years
Depreciation method:	sum-of-the-years-digit
Investment tax credit:	20% of total depreciable investment

A.3 BASE PLANT COSTS

Capital and total annualized cost estimates were developed for base plants examined. ("Base plant" in this PCTM refers to a K-T based synfuel plant with fuel production capabilities but without pollution control devices.) The cost estimates were developed from information found in the open literature and adjusted to the bases used in this PCTM. Specifically, the literature data were 1) adjusted to delete the cost of pollution controls (to the extent those costs could be identified), 2) scaled to the plant capacities examined in the PCTM, and 3) escalated to a 1980 dollar basis.

A.3.1 Base Plant Capital Costs

The major source of cost data for the methanol synthesis base plant is an engineering study performed by the Ralph M. Parsons Company (6). The plant capacity examined in this manual is approximately 36 percent of the capacity examined in the Parsons study. After the identifiable pollution control costs were subtracted from the installed equipment costs (IEC) reported in Reference 6, the IEC was adjusted to the PCTM capacity by multiplying by 0.437. This factor equals 0.36 raised to the 0.8 power, which was considered appropriate because many parts of the plant in the Parsons study consisted of multiple (4 to 7) trains. Thus, the majority, but not all of the desired capacity reduction (and hence cost reduction) could be accomplished by eliminating one or more process trains. In the cases of the Fischer-Tropsch (F-T) and Mobil M-gasoline syntheses base plants, the same approach was used although capital costs associated with methanol synthesis in the Parsons study were adjusted to reflect differences in costs among the three synthesis operations based on other cost data sources (7, 8, 9, 10).

The resulting adjusted installed equipment costs (IEC) were then escalated to 1980 dollars using the Chemical Engineering (CE) plant cost annual index. Finally, the escalated IEC was used to compute the other elements of the total capital investment as outlined earlier in Section A.1. The resulting base plant capital cost estimates are summarized in Table A-4.

TABLE A-4. CAPITAL COSTS FOR UNCONTROLLED K-T BASED INDIRECT LIQUEFACTION PLANTS

Item	Capital Costs, 10^6 Dollars (1980 basis)		
	Methanol	Fischer-Tropsch	Mobil M-Gasoline
Installed cost	603	714	657
Contractors Overhead and Fee	18	21	20
Engineering and Construction	151	178	164
Contingency	121	143	131
Subtotal, Facility Cost	893	1056	972
Interest During Construction	201	238	220
Working Capital	17	20	17
Total Capital Investment	1111	1314	1209

A.3.2 Base Plant Annualized Costs

Total annualized costs for the base plants have been estimated as the sum of the total operating costs and annualized capital changes. The total operating costs are based upon the annual coal cost ($35.44/Mg) and cost estimates for "water, catalyst, and chemicals" and "other operating costs" presented for the K-T based methanol production facility examined in the Parsons study (6). Published operating cost estimates were scaled directly on the basis of plant capacity and escalated to 1980 dollars. Published cost estimates for "water, catalyst, and chemicals" and "other operating costs" relate specifically to a methanol production facility; however, no adjustment has been made for F-T and Mobil M-gasoline synthesis cases. Furthermore, it is not known if any adjustment is required since insufficient details of these estimates are available. Similarly, the annual operating costs for pollution control equipment have not been deducted from cost estimates for "water, catalyst, and chemicals" and "other operating costs" since insufficient details of these estimates are available to do so. Capital-related charges have been estimated as outlined earlier in Section A.2.

The resulting total annualized cost estimates for K-T base plants are summarized in Table A-5. It should be noted that annual coal costs and capital-related charges comprise about 84% of the total annualized cost. Therefore, uncertainties associated with estimated costs for "water, catalyst, and chemicals" and "other operating costs" are not expected to have a major impact on the estimated total annualized cost.

TABLE A-5. ANNUALIZED COSTS FOR K-T BASED INDIRECT LIQUEFACTION PLANTS*

Item	Annualized Cost, 10^6 Dollars Methanol	 Fischer-Tropsch	 Mobil M-Gasoline
Coal	98	114	95
Water, Catalyst, and Chemicals*	4	4	4
Other Operating Costs*	53	63	51
Total Operating Cost	155	181	150
Capital Charges	191	226	208
Total Annualized Cost	346	407	358

*Annual operating costs relating to "water, catalyst, and chemicals" and "other operating costs" are based upon published cost estimates for a K-T based methanol production facility (6). Insufficient details were available to enable adjustment, if any is required, for F-T and Mobil M-gasoline synthesis cases or to deduct the annual operating costs for pollution controls.

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APPENDIX B

RECTISOL ACID GAS REMOVAL PROCESS

B.1 PROCESS DESCRIPTION

Rectisol is an acid gas removal process which removes carbon dioxide, hydrogen sulfide, carbonyl sulfide, organic sulfur compounds, hydrogen cyanide, ammonia, benzene, and gum-forming hydrocarbons from synthesis gases by means of physical absorption in an organic solvent (especially cold methanol) at temperatures below 273K. Operation is based upon the fact that these compounds, particularly the reduced sulfur species and carbon dioxide, are very soluble at high pressure in cold methanol and are readily recoverable by flash desorption. This is demonstrated in Figure B-1, which presents carbon dioxide solubility as a function of partial pressure (1). Consider, for example, the absorption of carbon dioxide at a partial pressure of 1.0 MPa. From Figure B-1 it is evident that at least 90 percent of the dissolved carbon dioxide may be desorbed by isothermal flashing at methanol temperatures of 258K or lower.

Solubility data for compounds at a partial pressure of 0.1 MPa over methanol are presented in Figure B-2 (2). It should be noted that gas solubilities generally increase with increasing partial pressure but that solubility coefficients (the ratio of solubility to partial pressure) do not increase appreciably with pressure until partial pressures exceed 0.1 to 0.2 MPa. Solubility coefficients of hydrogen sulfide and carbon dioxide are seen to increase substantially with decreasing temperature while those of major product gases such as hydrogen, carbon monoxide, and methane are relatively temperature independent. For this reason, Rectisol absorption columns operate at low temperatures, typically in the range of 253 to 213K (1,3,4). Low temperature operation also reduces solvent losses by reducing the partial pressure of methanol in the product streams.

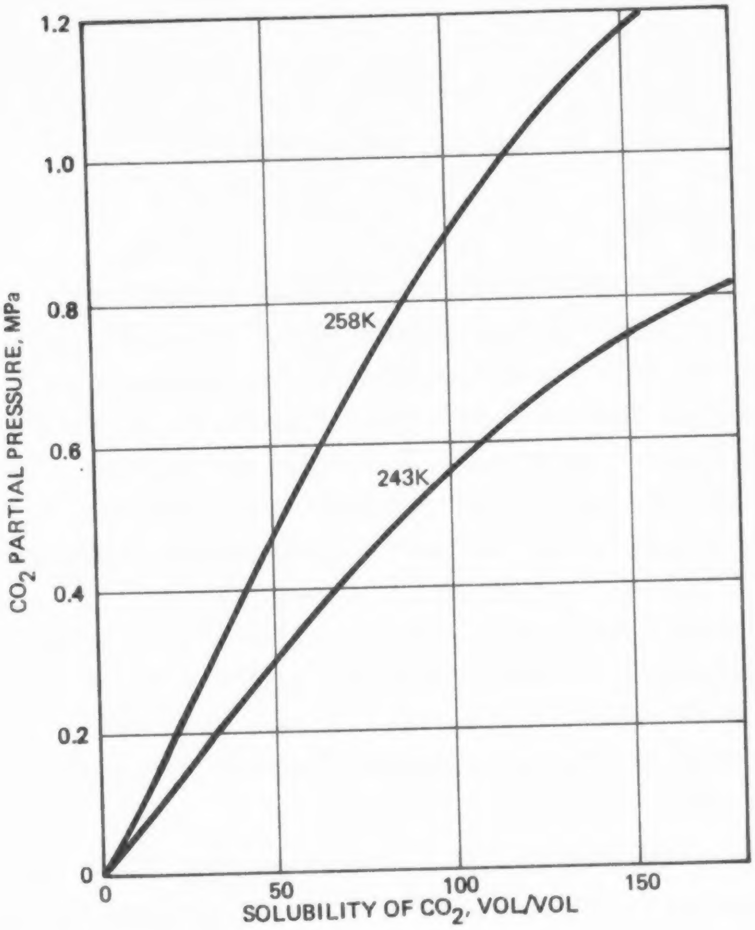

Figure B-1. Effect of partial pressure on solubility of carbon dioxide in methanol (1)

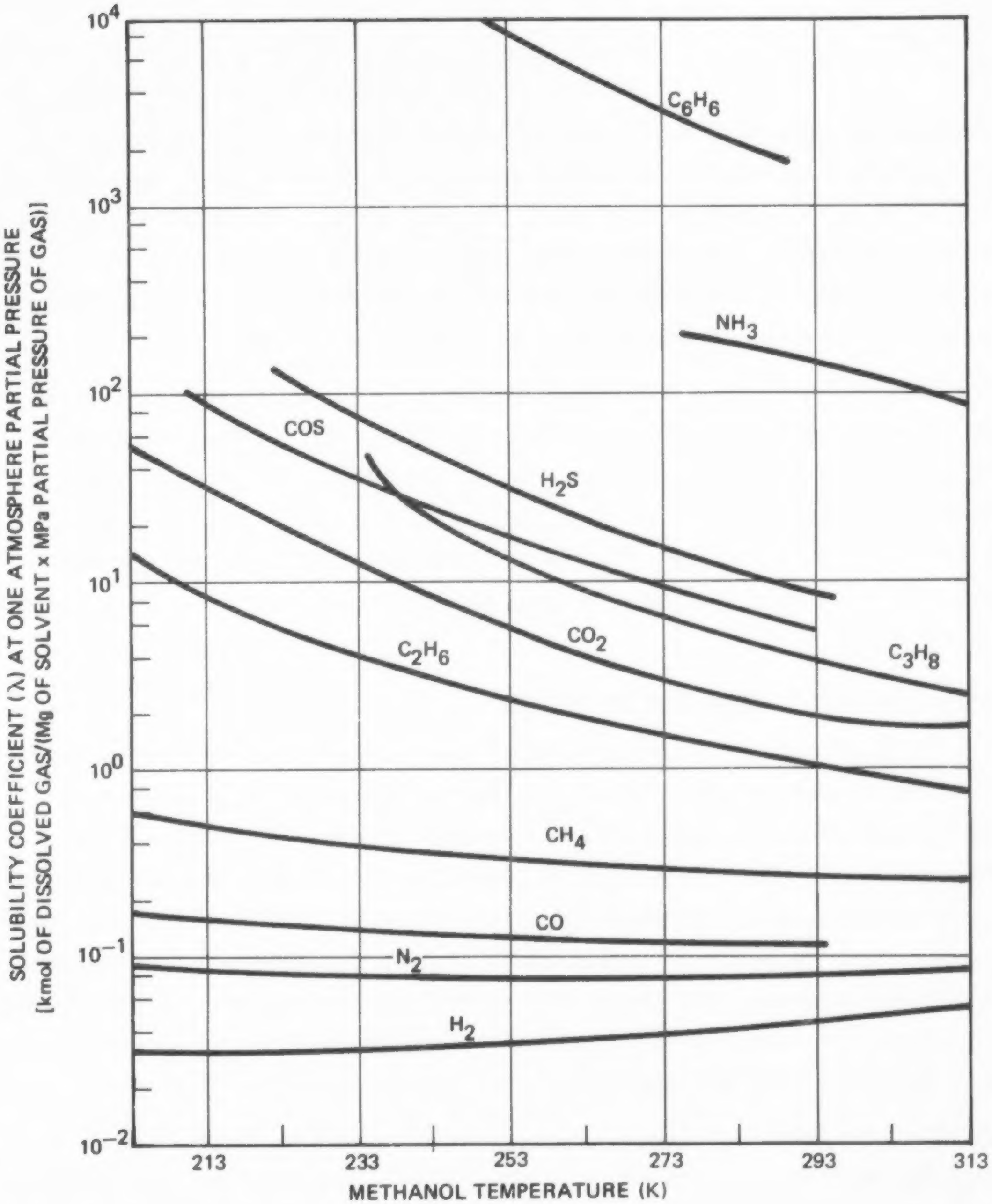

Figure B-2. Solubility of gases in methanol (2)

Because the solubilities of reduced sulfur species (e.g., hydrogen sulfide and carbonyl sulfide) in methanol are substantially greater than that of carbon dioxide at the same partial pressure, the Rectisol process is capable of selective recovery of reduced sulfur species versus carbon dioxide; to some degree, this holds for all physical absorption solvents capable of absorbing reduced sulfur species and carbon dioxide almost independently.

The Rectisol process was jointly developed by Linde Aktiengesellschaft (Munich, Germany) and Lurgi Mineralöltechnik (Frankfurt, Germany) and is currently licensed by both companies. It is also available through their U.S. subsidiaries, Lotepro Corp. (New York, NY) and Lurgi Corp. (River Edge, NJ), respectively. The Gelleschaft für Kohle Technologie (GKT, Essen, Germany) also has a limited Rectisol license applying to Koppers-Totzek (K-T) gasification facilities.

Selective Rectisol Process Configurations

A variety of selective Rectisol units are currently being used in applications such as ammonia and methanol synthesis, medium-Btu gas synthesis, natural gas purification, and refinery hydrogen production. Although selective Rectisol designs are site- and process-specific, common key features include low temperature operation, sequential hydrogen sulfide-carbon dioxide absorption, discrete methanol regeneration columns for hydrogen sulfide and carbon dioxide recovery, and separation of methanol and water by distillation. However, there are significant differences among the designs in use which relate to both the feed gas composition and the product specifications.

Examples of selective Rectisol process configurations used in coal gasification applications are presented in Figures B-3 and B-4. The process presented in Figure B-3 is used by AECI limited in Modderfontein, Republic of South Africa, and desulfurizes an essentially hydrocarbon-free quenched K-T gas prior to carbon monoxide shift conversion and subsequent carbon dioxide removal (5,6). Methanol is added to the feed gas prior to cooling and hydrogen

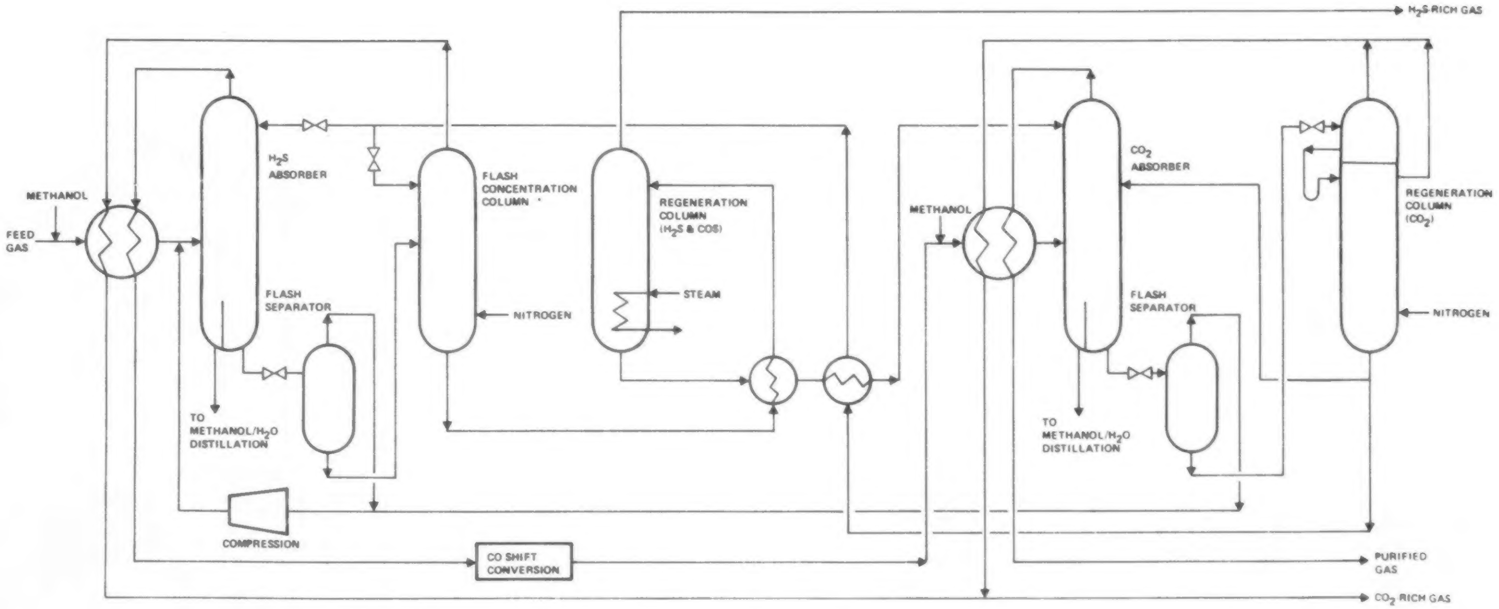

Figure B-3. Process flow diagram of the Modderfontein selective Rectisol system (5,6)

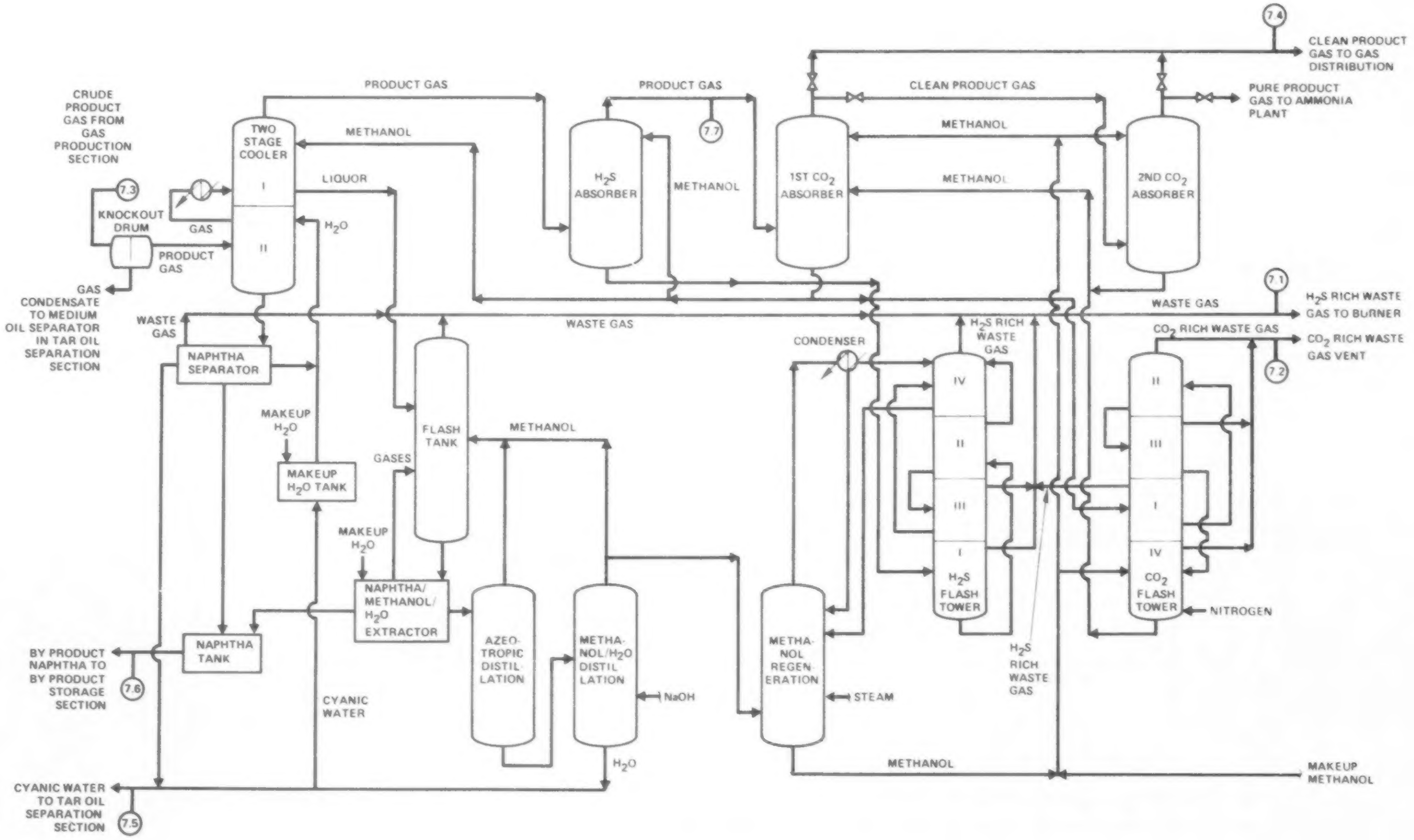

Figure B-4. Process flow diagram of the Kosovo selective Rectisol section (7,8) sulfide absorption to prevent icing. Moisture in the feed gas is removed from the hydrogen sulfide absorber in solution with methanol, which is recovered by distillation. Hydrogen sulfide and carbonyl sulfide are absorbed from the feed gas using sulfur-free methanol from the carbon dioxide regeneration column. Rich methanol from the hydrogen sulfide absorber is partially flashed to liberate absorbed hydrogen and carbon monoxide which is compressed and combined with the cold feed gas. Additional flashing and stripping in the concentration column, with re-absorption of reduced sulfur species in sulfur-free methanol, produces a sulfur-rich methanol stream for hot regeneration and a carbon dioxide off-gas. Hydrogen sulfide is recovered by stripping with methanol vapor in the regeneration column.

Carbon dioxide is removed from shifted process gas by absorption in regenerated methanol. Methanol is added to the shift gas prior to cooling and carbon dioxide absoprtion to prevent icing, and moisture in the shift gas is removed from the carbon dioxide absorber in solution with methanol. Rich methanol from the carbon dioxide absorber is partially flashed to recover absorbed hydrogen which is compressed and combined with the cold feed gas to the hydrogen sulfide absorber. Carbon dioxide is recovered by flashing and stripping with nitrogen in the carbon dioxide regeneration column.

It should be noted that desulfurization prior to shift conversion enables the use of conventional shift catalysts (e.g., iron-chromium and copper-zinc) and facilitates process selectivity by absorbing hydrogen sulfide in the presence of a minimum of carbon dioxide (approximately 10 to 12% by volume for K-T coal gasification, 18 to 20% for Texaco coal gasification, and 5 to 6% for gas produced by partial oxidation of oil). However, in conjunction with partial oxidation of liquid hydrocarbons for hydrogen or ammonia production, shift conversion employing sulfur tolerant cobalt-molybdate shift catalysts often precedes acid gas removal. Selective Rectisol configurations for such systems are similar to that presented in Figure B-3 except that no gas processing occurs between hydrogen sulfide absorption and carbon dioxide absorption. Shift conversion prior to acid gas removal results in an increased concentration of carbon dioxide in the hydrogen sulfide absorber feed gas (up to about 42 percent by volume). Owing to the less favorable carbon dioxide to hydrogen sulfide ratio after shift conversion, a greater degree of methanol enrichment is required to achieve the same selectivity attainable with an unshifted feed gas.

The process presented in Figure B-4 is used at the Kosovo Gasification Plant near Pristina, Yugoslavia for the production of medium Btu fuel gas and hydrogen for ammonia synthesis (7,8). Feed gas to the Rectisol unit is generated by gasification of lignite in oxygen-blown Lurgi gasifiers. Cooled crude product gas from gasification is further cooled by sequential washing with cold water and methanol in the two stage cooler. Condensed gas liquor from the water wash section is flashed to liberate dissolved sour gases, and the organic phase is recovered from wash water in the naphtha separator. Condensed gas liquor from the cold methanol wash section is flashed, and methanol and condensed moisture are recovered from the naphtha phase by extraction with water. Dissolved organics in the aqueous phase are recovered by distillation. Naphtha from the naphtha separator and the naphtha/methanol/water extractor is sent to by-product storage via the naphtha surge tank. Cyanic water from naphtha separation and methanol/water distillation is sent to tar/oil separation.

Product gas from the two stage cooler is scrubbed with carbon dioxide-rich methanol in the hydrogen sulfide absorber for bulk removal of reduced sulfur species. Carbon dioxide is removed from the first absorber top gas in two carbon dioxide absorbers. Bulk carbon dioxide removal is achieved in the first absorber by washing with carbon dioxide-lean methanol and regenerated methanol. Overhead gas from the first carbon dioxide absorber is fed directly into the fuel gas distribution system. When a higher purity gas is required for feed to the cryogenic hydrogen separation unit, additional carbon dioxide removal is achieved in the second carbon dioxide absorber using regenerated methanol.

Hydrogen sulfide-rich methanol is regenerated by multi-stage flashing in the hydrogen sulfide flash tower, and steam stripping in the methanol regeneration column. Hydrogen sulfide-rich waste gas from methanol regeneration is combined with flash gas from the naphtha separator and the methanol pre-wash flash tank prior to disposal. Carbon dioxide-rich methanol is regenerated by multi-stage flashing and nitrogen stripping in the carbon dioxide flash tower.

Based upon publicly available data, it is not known how the Kosovo Rectisol design compares with other selective Rectisol units currently processing Lurgi crude gas. Several selective Rectisol designs have been prepared for proposed Lurgi gasification facilities in the United States (e.g., facilities for Wesco, El Paso Natural Gas Co., Hampshire Energy Co., and Nakota Co.) (9). However, data with respect to process configuration are generally proprietary.

Configurations of the two units presented in Figures B-3 and B-4 differ in several respects. Principal differences result from (1) the fact that Lurgi crude gas contains significant levels of condensible hydrocarbons (approximately 0.01 kg C_{5+} aliphatics, benzene, toluene, and other aromatics per kg MAF coal) which must be removed prior to acid gas removal (10), (2) the need for two-stage acid gas removal if sulfur intolerant catalysts are used for shift conversion, and (3) the fact that at Kosovo all hydrogen sulfide containing offgases are simply burned so that high sulfide concentrations are not necessary as would be the case for Claus processing. Differences in the performance of these two units are detailed in Section B.3.

Non-Selective Rectisol Process Configurations

Non-selective Rectisol processes differ from selective processes in that all acid gas constituents are absorbed simultaneously and no carbon dioxide regenerator or reabsorber is used to produce high pruity carbon dioxide vent gas. An example of a commercial non-selective Rectisol unit is presented in

Figure B-5 which is a simplified schematic of the South African Oil, Coal and Gas Corporation's Sasol I acid gas removal system (1). Feed gas to acid gas removal is crude or partially shifted Lurgi gas from Fischer-Tropsch synthesis. The feed gas is split into three streams which are cooled in each of two stages by refrigeration, heat exchange with cold high pressure flash gas (including carbon dioxide-rich flash gases above 100 kPa), and heat exchange with cold product gas. Condensed moisture and hydrocarbons are recovered from the combined feed gas following the first cooling stage, and methanol is added to prevent icing in the second gas cooling stage. Following the second gas cooling stage, the condensed gas liquor is recovered from the coal gas and sent to the naphtha separator for by-product and methanol recovery.

Cooled gas is washed with cold methanol in three consecutive stages. In the first absorption or prewash stage, the cooled gas is washed with flashed methanol from the expansion tower to remove the final traces of condensible organics along with some hydrogen sulfide, carbon dioxide, and organic sulfur compounds. Rich methanol from the first stage absorber is combined with gas liquor from the second gas cooling stage and sent to the naphtha separator. Separator feed is flashed and extracted with water to yield an aqueous methanol phase and a by-product naphtha phase containing organic sulful compounds. Methanol is recovered from the aqueous phase by distillation.

Bulk acid gas removal is achieved in the second or main wash stage or absorption by washing with flashed methanol from the expansion tower. Rich methanol from the second stage absorber is regenerated along with the methanol/water still overhead in an expansion tower. Regeneration is by pressure reduction in six stages to a final pressure of about 30 KPa. High pressure flash gas consisting primarily of carbon dioxide, carbon monoxide, and hydrogen is used to cool the Rectisol feed gas and then used as on-site fuel gas. Low pressure flash gas is compressed and flared.

The third or finewash stage absorber effects final gas purification by washing the second stage absorber effluent gas with completely stripped

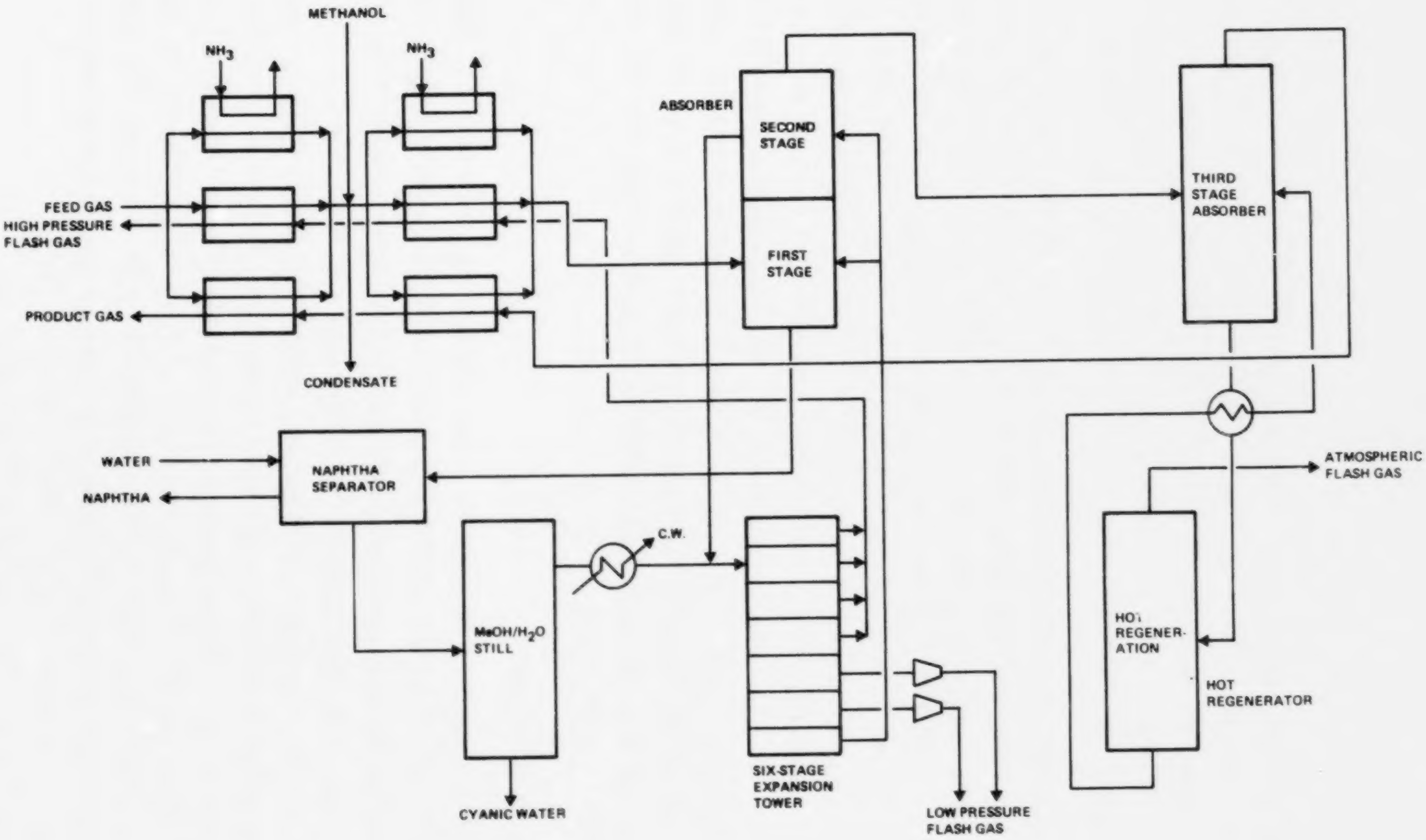

Figure B-5. Process flow diagram of the Sasol I non-selective Rectisol section (1) methanol from the hot regenerator. Rich methanol from the third stage absorber is partly regenerated by flashing to atmospheric pressure and then completely stripped of acid gas in a distillation column. Atmospheric flash gas from the hot regenerator is released for incineration. Cold product gas is used to precool the Rectisol feed gas and then sent to liquid synthesis.

Based upon publicly available data, it is not known how the Sasol I Rectisol design compares with other commercial non-selective Rectisol processes, although a similar design has been used in the Sasol II facility which was commissioned in 1980 (11). Non-selective Rectisol designs have been prepared for several proposed Lurgi gasification facilities in the United States including those proposed by Great Plains Gasification Associates (currently under construction), Wycoalgas Inc., Tenneco Coal Gasification, and El Paso Natural Gas Co. (9,12). A schematic of the Great Plains non-selective Rectisol section is presented in Figure B-6 (13). This schematic indicates a similar configuration to that of the Sasol I facility but includes details such as the prewash flash vessel and the azeotrope distillation column which are not included in Figure B-5.

B.2 PROCESS APPLICABILITY

The Rectisol process is used in three typical applications: 1) Removal of carbon dioxide, hydrogen sulfide, carbonyl sulfide, organic sulfur compounds, hydrogen cyanide, ammonia, benzene, and gum-forming hydrocarbons from crude gas produced by coal gasification for syngas and SNG production; 2) Removal of hydrogen sulfide, carbonyl sulfide, and carbon dioxide from gas produced by partial oxidation for syngas or hydrogen production; 3) used in conjunction with low temperature liquefaction and fractionation plants for removal of acidic components present at moderate levels. Process limitations in these applications primarily relate to requirements for high pressure, low temperature operation and methanol contamination by minor constituents present in the feed gas.

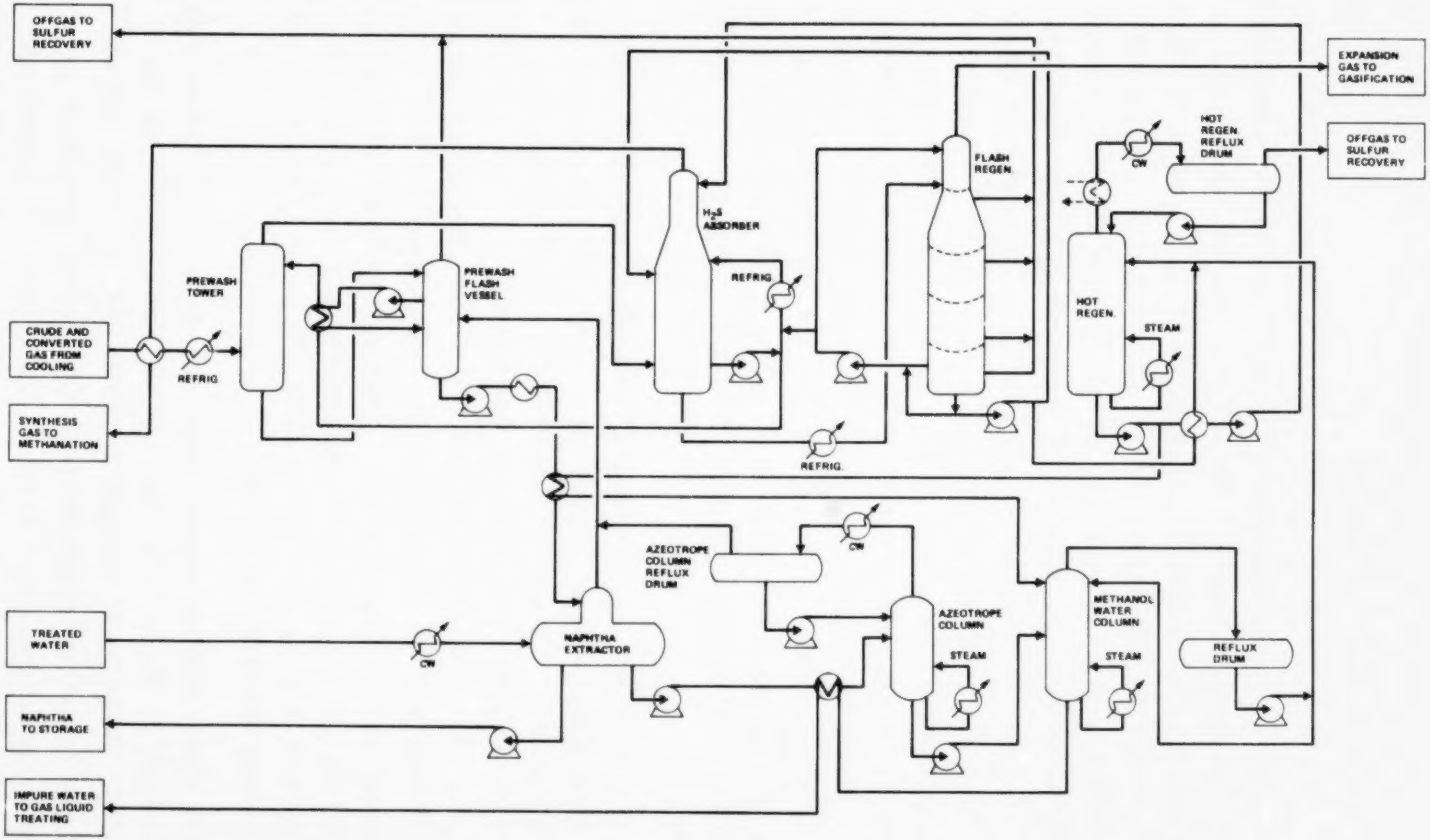

Figure B-6. Process flow diagram of the Great Plains non-selective Rectisol section (13)

As with any other physical absorption process, the minimum circulation rate of solvent required for complete removal of a gaseous constituent is inversely proportional to the partial pressure of the constituent in the feed gas and to the solubility coefficient for the constituent in the solvent used. Process economics depend mainly upon the solvent circulation rate because the circulation rate influences the size of all equipment and, therefore, the capital costs. Solvent circulation rate also affects the operating costs since pumping costs are proportional to circulation rate and regeneration costs are nearly proportional to the circulation rate (14). Therefore, the economics of physical absorption processes improves with increasing acid gas partial pressures. Physical solvent type acid gas removal processes are typically selected when acid gas partial pressures are greater than about 1.0 to 1.4 MPa (1, 15). Feed acid gas partial pressures at existing Rectisol units in coal gasification and partial oxidation applications are in the range of 0.4 to 2.6 MPa (3,5,6).

As indicated in Figure B-2, the solubilities of most gases of interest increase with decreasing methanol temperature. Thus, for reasons mentioned above, Rectisol economics improve with decreasing methanol temperature. Rectisol absorption columns operate at low temperatures, typically in the range of 253 to 213K (1,3,4). An additional benefit of low temperature operation is the attendant reduction of methanol losses. Vapor pressure data for methanol are presented in Figure B-7 (1). These data indicate that methanol losses can be decreased by a factor of about three to four for each 20K temperature reduction down to 253K and by about one order of magnitude for each 20K temperature reduction below 253K.

Minor constituents such as ammonia, hydrogen cyanide, and nitrogen oxides which may be present in the Rectisol feed gas can complicate operation or result in fouling. Ammonia and hydrogen cyanide, which are very soluble in methanol, make the regeneration process more complicated and result in additional steam requirements (2). Further, the presence of ammonia and

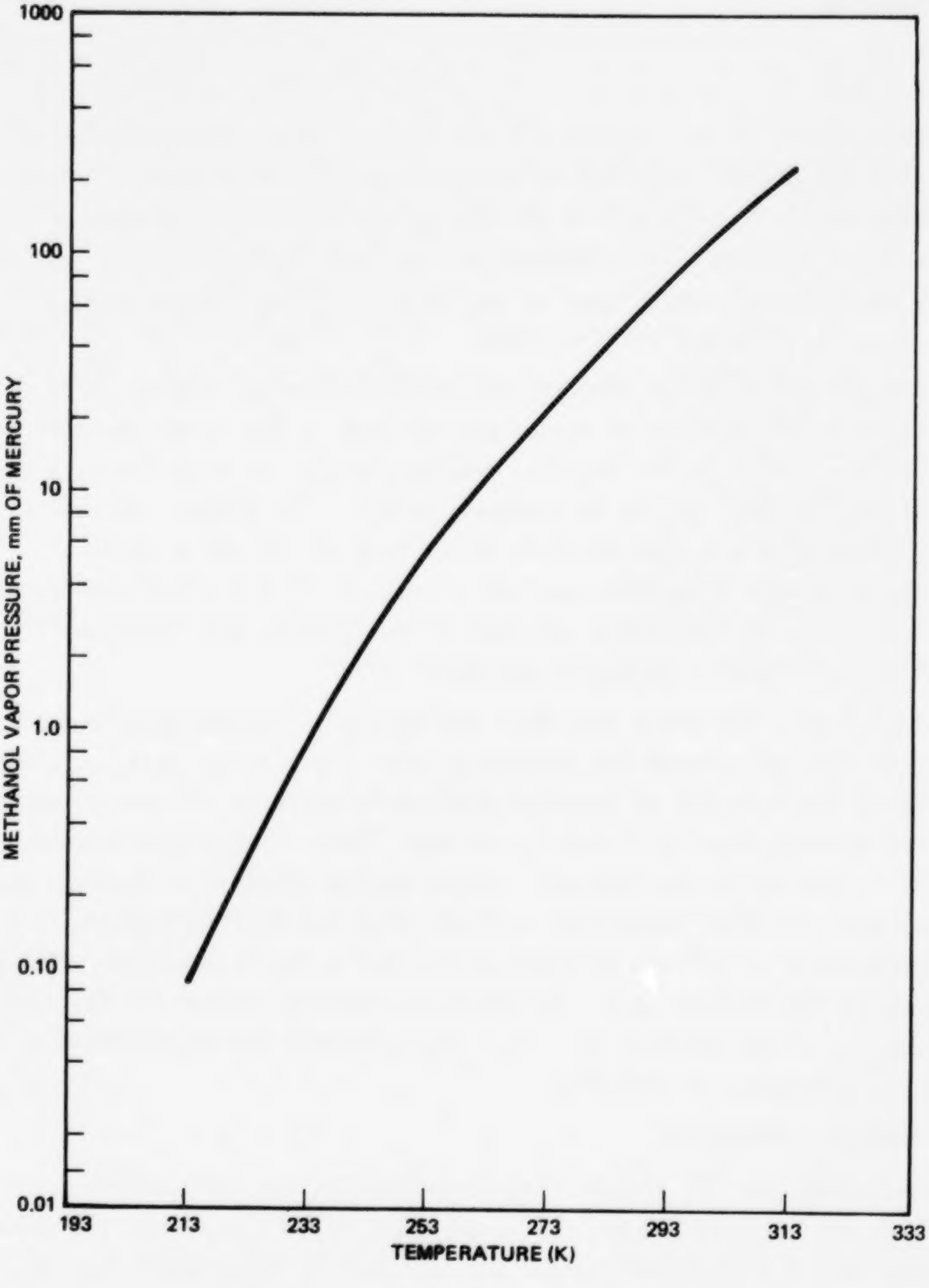

Figure B-7. Vapor pressure of methanol (1) hydrogen cyanide in the hydrogen sulfide fraction is not desirable due to the potential for adverse reactions during subsequent sulfur recovery. These contaminants may be removed from the feed gas by employing a prewash of either cold water or methanol. This prewash also provides feed gas drying (particularly the methanol prewash) and, in low temperature gasification applications, removes condensible hydrocarbons.

One coal gasification facility has reported Rectisol fouling which is attributed to the presence of oxygen and nitrogen oxides in the Rectisol feed gas (16,21). Oxygen in the Rectisol feed gas results in oxidation of a portion of the hydrogen sulfide to elemental sulfur. The presence of nitric oxide in addition to oxygen accelerates the rate of sulfide oxidation. Deposits of sulfur in columns resulted in reduced solvent circulation rates, and fouling of heat exchangers resulted in insufficient cooling capability to achieve the required degree of gas purification.

It has been determined that this fouling can be reduced by allowing low levels of hydrogen cyanide and ammonia to enter the Rectisol unit to solubilize sulfur by formation of ammonium thiocyanate which is ultimately removed with the methanol/water distillation bottoms. When insufficient hydrogen cyanide is present in the feed gas, sodium cyanide solution is injected into the methanol. A more fundamental solution which has been implemented is the hydrogenation of oxygen and nitrogen oxides over a cobalt molybdate catalyst upstream of the Rectisol unit. Formation of elemental sulfur and the associated fouling of the Rectisol unit have not occurred since installation of the catalytic hydrogenation unit (21).

B.3 PROCESS PERFORMANCE

Depending upon the product requirements and other site specific constraints, the Rectisol process can be designed to yield a product gas containing less than 0.1 ppmv total sulfur and less than 10 ppmv carbon dioxide. The carbon dioxide content achievable in the purified gas is independent of the type of Rectisol process employed (e.g., selective or non-selective Rectisol). However, in the case of a non-selective Rectisol process, the utilities (steam, cooling water, and refrigerant) would increase to obtain a product gas with ppmv levels of carbon dioxide. Publicly available data indicate that in gasification applications involving an essentially hydrocarbon-free feed gas, selective Rectisol processes can produce a sulfur-rich offgas containing 25-75% hydrogen sulfide and a carbon dioxide-rich offgas containing less than 10 ppmv total sulfur. The presence of moderate quantities of hydrocarbons in the feed gas (9 to 16 percent) has no influence on the selectivity of hydrogen sulfide recovery; hydrogen sulfide concentrations of 25 to 35 percent in the hydrogen sulfide-rich offgas can be achieved along with a carbon dioxide-rich offgas containing 10 ppmv total sulfur. However, C_3 and C_4 hydrocarbons present in the feed gas will tend to concentrate in the hydrogen sulfide-rich offgas.

Performance data for selective Rectisol units treating essentially hydrocarbon free feed gases are summarized in Table B-1. Plants 1 and 2 produce hydrogen and ammonia synthesis gas, respectively, by partial oxidation of oil. These plants utilize sulfur tolerant shift conversion catalysts which enable shift conversion prior to acid gas removal. Therefore, the feed gases to Plants 1 and 2 contain 31 to 35% carbon dioxide, 62-64% hydrogen, and less than about 5% carbon monoxide (2,3,6,17). Plant 3 is a coal gasification facility producing ammonia synthesis gas. This plant employs a two-stage Rectisol system which removes sulfur species prior to shift conversion and removes carbon dioxide subsequent to shift conversion (refer to Figure B-3 for example process flow diagram). Feed gas to the Plant 3 sulfur absorber therefore contains only 12-13% carbon dioxide, 27-29% hydrogen and about 57% carbon monoxide (2,6). Feed gas to the carbon dioxide absorber in Plant 3, which is not included in Table B-1, contains 42-43% carbon dioxide, 53-54% hydrogen, and about 3% carbon monoxide.

TABLE B-1. SELECTIVE RECTISOL PERFORMANCE DATA FOR HIGH TEMPERATURE GASIFICATION APPLICATIONS[*]

Gas	Feed Gas, Mole %			Purified Gas, Mole %			Stripping Gas, Mole %			CO_2-Rich Offgas, Mole %			H_2S-Rich Offgas, Mole		
Component	Plant 1	Plant 2	Plant 3	Plant 1	Plant 2	Plant 3	Plant 1	Plant 2	Plant 3	Plant 1	Plant 2	Plant 3[‡]	Plant 1	Plant 2	Plant 3
H_2	62.35-63.74	61.59	27.5-29.3	93.58-94.08	94.92	93.0-93.2				0.31-0.33	0.76	0.40-0.44	-	-	-
N_2+Ar	0.12 - 0.52	0.41	1.52	0.17 - 0.82	0.67	1.78	100	100	100	17.2-19.3	8.22	12.1 - 14.5	0.08	1.92	2.5 - 8.4
CO	3.24-4.13	2.60	56.62	4.86	3.94	4.97-5.15				0.08-0.14	0.11	0.34 0.43	-	-	-
CH_4	0.13-0.17	0.33	0.10	0.19 0.24	0.47	0.10				≤0.02	0.06	0.01	-	-	-
CO_2	31.62-33.23	34.55	11.8-13.3	≤10ppm	50ppm	≤50ppm				80.2-82.4	90.85	84.7-87.0	64.7-74.7	68.31	10.6-71.9
H_2S	0.26-0.49	0.52	0.59-0.75	≤1ppm	1ppm	<2ppm				2-5ppm	5ppm	<5ppm	25.2-35.1	29.77	25.5-71.9[†]
COS	10-63ppm	-	0.10	-	-	-				8ppm	-	<2ppm	0.08-0.76	-	9.54[§]
Flow Rate, kmol/hr	3562-3992	6112	4691-4801	2426-2639	3950	4078-4096	266	187	334-543	1370-1567	2243	2731-3690	30-55	107	48-108
Temperature, K	303-313	-	311	295-309	-	304	303	-	311	295-303	-	302	303-322	-	311
Pressure, MPa	3.2-3.3	7.3	3.0-3.1	2.9-3.1	7.1	4.8	0.25	0.49	0.26-0.44	0.10	0.11	0.097	0.40-0.44	0.19	0.24-0.26

[*] Plant 1 is a refinery producing hydrogen by partial oxidation of oil; shift conversion occurs prior to acid gas removal (2,6,17).
Plant 2 produces ammonia synthesis gas from crude hydrogen generated by partial oxidation of oil; shift conversion occurs prior to acid gas removal (3).
Plant 3 produces ammonia synthesis gas by coal gasification; shift conversion follows hydrogen sulfide removal but precedes carbon dioxide removal (2,6). Refer to Figure B-3 for example process flow diagram. Sulfur-free gas is compressed prior to shift conversion.

[†] Higher hydrogen sulfide concentrations require more refrigeration and more stripping gas.

[‡] Concentrations of HCN and NH_3 in the CO_2-rich offgas at Plant 3 are 14 ppmv and 12 ppmv, respectively (5,6).

[§] A COS level of about 3.4 mole percent would be expected with an H_2S concentration of 25.5 mole percent.

These selective Rectisol units are seen to perform similarly in most respects over a wide range of operating pressures although there is a substantial range in the concentration of hydrogen sulfide, 25-72%, in the sulfur-rich waste gas from Plant 3. Lotepro Corporation has indicated that the higher hydrogen sulfide concentration is attainable at the expense of higher refrigeration and stripping gas requirements (6). The amount of stripping gas is a function of the hydrogen sulfide concentration desired in the hydrogen sulfide-rich offgas, the type of Rectisol process, the feed gas pressure, and the carbon dioxide, hydrogen sulfide, and carbonyl sulfide concentrations in the feed gas. Under given conditions an increase in stripping gas of about 60% is necessary to increase the hydrogen sulfide concentration from 25-70%.

Performance data for the Kosovo selective Rectisol unit (taken at partial load and not fully representative of normal performance), which treats crude gas from Lurgi gasification, are summarized in Table B-2 (refer to Figure B-4 for the process flow diagram). Data were obtained during three sampling campaigns in the period of September 1977 to November 1978. Tabulated data represent the best overall data obtained during these tests, and the ranges of the available data. As indicated previously, the presence of moderate levels of hydrocarbons in the feed gas has no influence on process selectivity. Differences in process selectivities indicated in Tables B-1 and B-2 primarily reflect differences in process requirements. At the Kosovo facility, the sulfur-containing gases are burned, and, therefore, high sulfur concentrations in these offgases are not necessary. Thus, unlike the facilities cited in Table B-1, the Kosovo facility does not utilize an enrichment stage. Also, Kosovo's hydrogen and methane rich flash gases from the carbon dioxide and hydrogen sulfide loaded methanol streams are added to the hydrogen sulfide fraction rather than being recycled to the feed gas.

Available performance data for the Sasol I non-selective Rectisol unit, which also treats crude gas from Lurgi gasification, are presented in Table

TABLE B-2. SELECTIVE RECTISOL PERFORMANCE DATA FOR LURGI (KOSOVO) MEDIUM-BTU GASIFICATION (7,18)*

Gas Component	Crude Product Gas (Stream 7.3), mole Value⁺	Crude Product Gas (Stream 7.3), mole Range	Clean Product Gas (Stream 7.4), mole Value⁺	Clean Product Gas (Stream 7.4), mole Range	CO_2-Rich Waste Gas (Stream 7.2), mole Value⁺	CO_2-Rich Waste Gas (Stream 7.2), mole Range	H_2S-Rich Waste Gas (Stream 7.1), mole Value⁺	H_2S-Rich Waste Gas (Stream 7.1), mole Range	Cyanic Water (Stream 7.5) Value⁺	Cyanic Water (Stream 7.5) Range
H_2	38.1	36-46	60	59-67	~0.01	<0.01-0.8	0.11	0.02-0.11		
O_2	0.36	0.09-2.6	0.44	0.1-1.7	~0.01	~0.01-1.8	~0.01	~0.01-0.51		
N_2	0.64	0.04-1.6	0.38	0.32-6.8	~0.01	~0.01-48	~0.01	~0.01-3.2		
CO	15	9.6-17	22	13-23	~0.01	<0.01- 0.01	1.1	1.1-3.5		
CO_2	32	21-40	0.02	<0.01-2.4	94	91-95	88	85-92		
CH_4	11.5	8.9-14.5	16	12-18	1.2	0.6-1.8	4.3	4.1-4.7		
C_2H_6	0.47	~1ppmv-0.76	0.15	~1ppmv-0.18	1.6	0.29-1.6	0.82	0.34-0.97		
C_2H_4	0.04	~1ppmv-0.11	~1ppmv	--	~1ppmv	--	~1ppmv	--		
C_3	0.19	0.07-0.40	~1ppmv	~1ppmv-0.09	0.28	0.17-0.55	0.63	0.22-1.1		
C_4	0.074	0.02-0.24	~1ppmv	--	~1ppmv	<1ppmv-0.23	0.32	0.14-0.58		
C_5	0.044	0.01-0.06	~1ppmv	--	~1ppmv	1ppmv-0.17	0.04	0.03-0.21		
C_6^+	0.064	0.02-0.20	0.03	<1ppmv-0.03	<1ppmv	--	0.21	0.01-0.22		
Benzene	750ppmv	660-840ppmv	--	--	1ppmv	--	110ppmv	40-110ppmv		
Toluene	230ppmv	200-260ppmv	--	--	~1ppmv	--	8ppmv	4-8ppmv		
Xylene and Ethylbenzene	100ppmv	16-110ppmv	--	--	~1ppmv	--	<1ppmv	--		
Phenols	~1ppmv	--	~1ppmv	--	1ppmv	--	~1ppmv	--		
H_2S	0.60	0.44-0.78	<1ppmv	--	39ppmv	20-90ppmv	4.54	1.6-5.0		
COS	97ppmv	63-120ppmv	0.17ppmv	<1-0.2ppmv	62ppmv	~1-62ppmv	420ppmv	360-540ppmv		
CH_3SH	590ppmv	460-700ppmv	1.1ppmv	~1-1.9ppmv	8.5ppmv	8.2-9.7ppmv	0.21	0.19-0.48		
C_2H_5SH	200ppmv	98-270ppmv	1.0ppmv	~1-1.7ppmv	4.4ppmv	3.4-6.1ppmv	780ppmv	670-850ppmv		
NH_3	3.3ppmv	<1-3.3ppmv	~1ppmv	<1-30ppmv	4.6ppmv	1-4.6ppmv	0.22	<1ppmv-0.22		
HCN	320ppmv	60-320ppmv	--	--	13ppmv		200ppmv	83-200ppmv		
pH									11.9	11.4-12.1
Total Solids, mg/L									7.30	--
Total Nonvolatile Solids, mg/L									450	--
Total Suspended Solids, mg/L									140	--
Total Dissolved Solids, mg/L									590	--
COD (as mgO_2/L)										
Permanganate (as mgO_2/L)									205	--
Total Sulfur, mg/L									570	--
Flow Rate, kmol/hr	703		491		90		102		60	52-68
Flow Rate, m^3/hr									0.8	--
Temperature, K	295	293-295	--	--	292	--	285		353	--

***Refer to Figure B-4 for process flow diagram.**

⁺Values are best overall values from available data .

B-3 (refer to Figure B-5 for the process flow diagram). As initially designed, the high pressure flash gas is used as an on-site fuel gas, the low pressure flash gas is flared, and the atmospheric flash gas is vented to the atmosphere through the power stack (19). More recently, a Stretford unit was designed to treat the atmospheric flash gas which contains about 90% of the sulfur species absorbed (17,19). Proposed designs for U.S. facilities indicate that at least a portion of the high pressure flash gas stream is recycled to the gasification plant for recovery of carbon monoxide, hydrogen, and methane; some fraction of the high pressure flash gas may be combined with the other waste gases for sulfur recovery (12,20). Therefore, the performance indicated in Table B-3 may require some adjustment.

B.4 RECTISOL WASTE STREAMS

Secondary waste streams produced by the Rectisol acid gas removal process are: (1) hydrogen sulfide-rich offgases, (2) carbon dioxide-rich offgases (selective Rectisol processes only), and (3) methanol/water distillation bottoms. Available characterization data for the offgas streams have been summarized in Section B.3 for each of the three basic Rectisol process configurations. The sulfur-rich offgas is typically sent to the sulfur recovery unit, either Claus or Stretford, or flared. When the Rectisol process is used in conjunction with low temperature coal gasification systems (e.g., Lurgi gasifiers) the Rectisol feed gas contains significant concentrations of C_2^+ hydrocarbons relative to the concentration of hydrogen sulfide. The naphtha fraction is recovered from the feed gas by washing prior to acid gas removal. Lighter hydrocarbons largely pass through the prewash and are, to some extent, absorbed with the acid gases. These light hydrocarbons, particularly the C_3s and C_4s, tend to concentrate in the hydrogen sulfide-rich offgas and may also be present in the carbon dioxide-rich offgas. Therefore, unless special precautions are taken, high levels of these C_3 and C_4 hydrocarbons in the Rectisol feed gas may result in off-color sulfur if Claus sulfur recovery is employed or excessive tail gas hydrocarbon emissions if

TABLE B-3. PERFORMANCE DATA FOR THE NON-SELECTIVE RECTISOL AT SASOL I (LURGI GASIFICATION)(17)*

Gas Component	Rectisol Feed Gas, Mole %	Product Gas, Mole %	Off-Gases, Mole % High Pressure Flash Gas	Off-Gases, Mole % Low Pressure Flash Gas	Off-Gases, Mole % Atmospheric Flash Gas
H_2	40.05	57.30	21.4	2.6	0.14
CO	20.20	28.40	18.2	4.8	0.0
CH_4	8.84	11.38	11.4	7.2	0.9
CO_2	28.78	0.93	46.7	83.4	97.2
N_2+Ar	1.59	1.77	1.5	0.8	0.03
H_2S	0.30	ND	0.32	0.49	0.88
COS	10ppmv	NA	NA	NA	30ppmv
CS_2	NA	NA	NA	NA	2ppmv
RSH	20ppmv	NA	NA	NA	280ppmv
Thiophene	NA	NA	NA	NA	2ppmv
Total sulfur	NA	0.04ppmv	NA	NA	NA
C_2^+	0.54	-	0.7	1.1	0.7
Flow Rate, NM^3/hr	381,000	263,000	4,600	15,000	98,000
Temperature, K	303	288	273	273	268
Pressure, MPa	2.6	2.4	1.3	0.48	0.11

*Refer to Figure B-5 for process flow diagram.

Stretford sulfur recovery is employed. An approach proposed in conjunction with Wesco and Hampshire Energy Co. selective Rectisol units involves the use of an amine unit (ADIP) to separate hydrocarbons from the Claus feed gas (9,20).

Carbon dioxide-rich offgas from selective Rectisol units is either sold as by-product or vented to the atmosphere at existing facilities. As discussed above, light hydrocarbons present in the Rectisol feed gas are coabsorbed to some extent with the acid gases and may be present in the carbon dioxide-rich offgas. Further, steps taken within the Rectisol process to minimize hydrocarbon levels in the hydrogen sulfide fraction will likely result in increased hydrocarbon levels in the carbon dioxide offgases. Similarly, carbon monoxide is coabsorbed and will be present in the carbon dioxide-rich offgas due to its low solubility in methanol. Of course the extent of carbon monoxide coabsorption, and therefore its potential concentration in the carbon dioxide-rich offgas, depends upon its partial pressure. Thus, for similar acid gas removal systems, processes requiring only partial shift conversion (e.g., SNG, methanol, or acetic acid syntheses) would be prone to higher concentrations of carbon monoxide in the carbon dioxide-rich offgas. Therefore, proposed designs in Lurgi-based coal gasification applications indicate either incineration of the carbon dioxide-rich offgas for control of hydrocarbon and carbon monoxide emissions, or sale of the offgas as by-product; direct discharge to the atmosphere is not proposed. Also, at least one non-Lurgi coal gasification plant currently under construction, the Tennessee Eastman Kingport, Tennessee Texaco gasification project, proposes catalytic incineration of a carbon monoxide enriched portion of the carbon dioxide offgas for control of carbon monoxide emissions (21).

Publicly available characterization data for the methanol/water distillation bottoms are extremely limited. This is apparently due to the fact that the size of the still bottoms stream is generally quite small relative to other wastewater streams requiring similar wastewater treatment (e.g., gas liquor and synthesis condensates). Thus, from an operational standpoint, the still bottoms are likely to be of minor significance other than for checking still operation and methanol losses. One set of data, provided by Sasol personnel (19), are presented in Table B-4. At the Sasol facility, this waste stream is sent directly to biological treatment where it comprises less than 2% of the feed to this system.

TABLE B-4. CHARACTERIZATION DATA FOR METHANOL/WATER DISTILLATION BOTTOMS AT SASOL (19)

Parameter/Component	Value
pH	9.7
Phenol, mg/L	18
Cyanides (as CN), mg/L	10.4 (includes thiocyanate)
Ammonia (as N), mg/L	42
Sulfides (as S)	Trace
COD, mg/L	1,686

B.5 PROCESS RELIABILITY

The original Lurgi non-selective Rectisol unit built at Sasol in 1955 has operated with an on-stream factor of about 97% (17). Normal maintenance includes partial shutdown about once per year for cleaning of critical equipment and complete shutdown every two years during the normal plant downtime. Major upsets in the Rectisol unit requiring process adjustments rarely occur (19).

As discussed in Section B.2, plugging problems in a two-stage selective Rectisol unit at a coal gasification facility have been reported (16). This problem has been attributed to deposition of elemental sulfur resulting from the presence of nitrogen oxides in the Rectisol feed gas. Fouling was at least partially controlled by allowing low levels of hydrogen cyanide and ammonia to enter the Rectisol unit to solubilize sulfur by formation of ammonium thiocyanate. A more fundamental solution is the hydrolysis of nitrogen oxides and oxygen over a cobalt molybdate catalyst ahead of the Rectisol unit. Detailed operating data from this facility are not available.

B.6 PROCESS ECONOMICS

Available capital costs and utility requirements for the Rectisol process are summarized in Tables B-5 and B-6, respectively. Tabulated capital costs are primarily conceptual design cost estimates while tabulated utility requirements are published data for existing units. It should be noted that the cost of a Rectisol unit is influenced by a variety of considerations including the feed gas flow rate and pressure, acid gas content, and heavy hydrocarbon content, and the desired levels of selectivity and product purity. Due to the number of variables and associated interdependencies of these variables which influence cost, costs of Rectisol systems tend to be highly case specific.

TABLE B-5. CAPITAL COSTS FOR RECTISOL ACID GAS REMOVAL UNITS

	Dry Feed Gas, kmol/hr	Total Pressure, MPa	CO_2, vol %	H_2S, vol %	Capital Cost, $\$10^6$ (adj. to 1980 basis)	Reference
Selective	6,100	7.8	35	0.25	13.5[*]	24
	96,384	2.9	28.9	0.250	150.6[†]	25
Non-Selective	52,786	2.8	31.4	0.135	91.8[‡]	23
	57,574	2.8	34.2	0.130	81.9[‡]	22

[*] The feed gas to this unit does not contain heavy hydrocarbons. Cost includes refrigeration unit, erection, and plant startup. This is the same unit which is identified as plant 5 in Table B-6.

[†] Data are based upon a conceptual design cost estimate. Details of the cost estimate are not available. The feed gas to this unit does not contain heavy hydrocarbons.

[‡] Data are based upon a conceptual design cost estimate. The feed gas to this unit contains heavy hydrocarbons. Reported cost includes naphtha and methanol recovery and erection. It is not specified whether the costs for a refrigeration unit and unit startup are included.

TABLE B-6. UTILITY REQUIREMENTS FOR RECTISOL ACID GAS REMOVAL UNITS

	Selective Rectisol*					Non-Selective Rectisol†
	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Flow Rate, kmol/hr	3692-3992	6112	7112	6350	6190	16993
Pressure, MPa	3.2-3.3	7.3	3.0	3.3	7.8	2.6
Electric Power, kW hr/kmol	0.14-0.15	0.31	0.18	0.57	0.168	No data
Low Pressure Steam, MJ/kmol	5.14-5.54	3.44	4.16	5.09	2.77	3.27
Cooling Water, MJ/kmol	1.20-1.42	6.43	1.92	9.52	1.91	0.682
Stripping Nitrogen, kmol/kmol	0.067-0.072	0.031	0.048	0.067	0.043	No data
Makeup Methanol, kg/kmol	0.0085-0.0092	0.0057	0.012	0.0079	0.007	0.013
Refrigeration, MJ/kmol (at 227 to 235K)	2.09-2.29	Included above in power and cooling water	1.90	Included above in power and cooling water	1.24	No data

*Plant 1 is a refinery producing hydrogen by partial oxidation of oil; shift conversion occurs prior to acid gas removal (2,6). Refer to Table B-1 for performance data.
Plant 2 produces ammonia synthesis gas from crude hydrogen generated by partial oxidation; shift conversion occurs prior to acid gas removal (3). Operating costs reflect the use of compression refrigeration. Refer to Table B-1 for performance data.
Plant 3 produces ammonia synthesis gas by coal gasification; shift conversion follows hydrogen sulfide removal but precedes carbon dioxide removal (2,6). After sulfur removal the gas is increased from 3 MPa to 5 MPa by compression; the additional power required for compression is not included in the tabulated electric power requirement. Tabulated data are based on gas flow rate after shift conversion. Refer to Figure B-3 for process flow diagram, and to Table B-1 for performance data.
Plant 4 uses a Rectisol unit for purification of hydrogen from partial oxidation of heavy crude oil; shift conversion occurs prior to acid gas removal (3).
Plant 5 produces ammonia synthesis gas by partial oxidation of oil; shift conversion occurs prior to acid gas removal. Approximately 62% of the incoming carbon dioxide is provided as a carbon dioxide fraction containing less than 1.5 ppmv sulfur for urea production (24).
†Plant 6 is the Sasol coal gasification facility (17). Refer to Figure B-5 for process flow diagram, and Table B-3 for performance data.

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